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EM Samples Under Pressure

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EM Samples Under Pressure

212 Ruska, Beitrag zur übermikroskopischen Abbildung bei höheren Drucken [Kolloid-Zeitschrift

Aus dem Laboratorium für Elektronenoptik der Siemens & Halske AG., Berlin-Siemensstadt.

Beitrag zur übermikroskopischen Abbildung bei höheren Drucken.

Von E. Ruska. (Eingegangen am 13. Mai 1942)

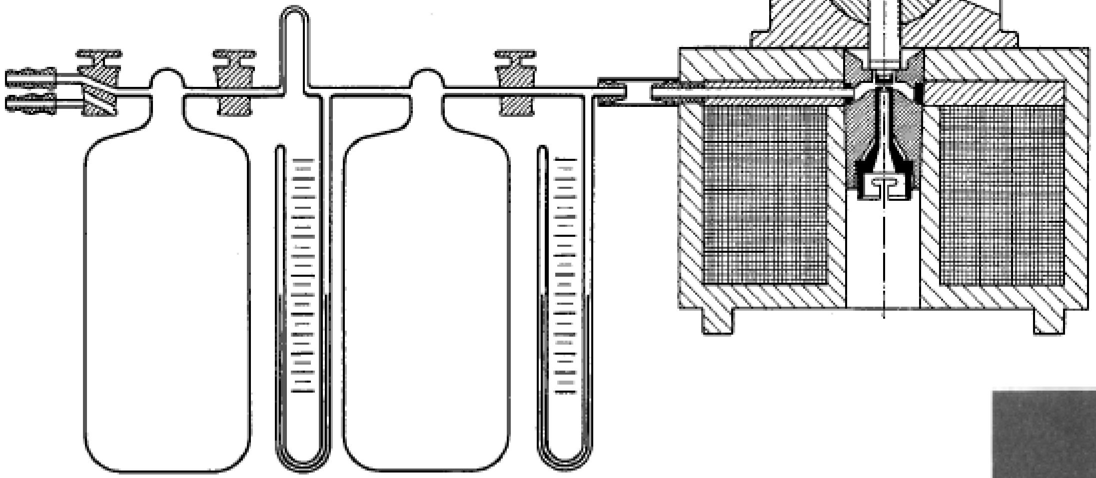


Fig. 1. Schematischer Querschnitt durch die Versuchsanordnung.

Does

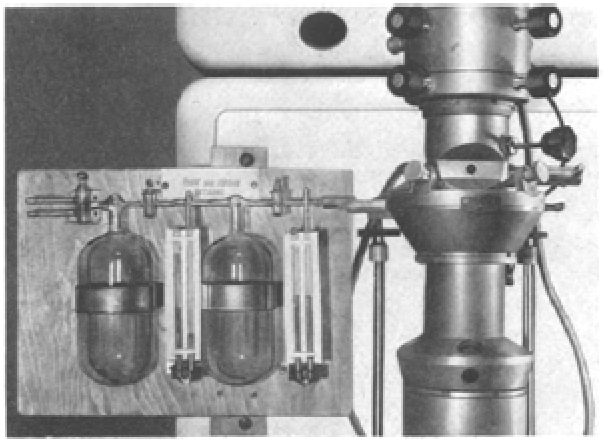
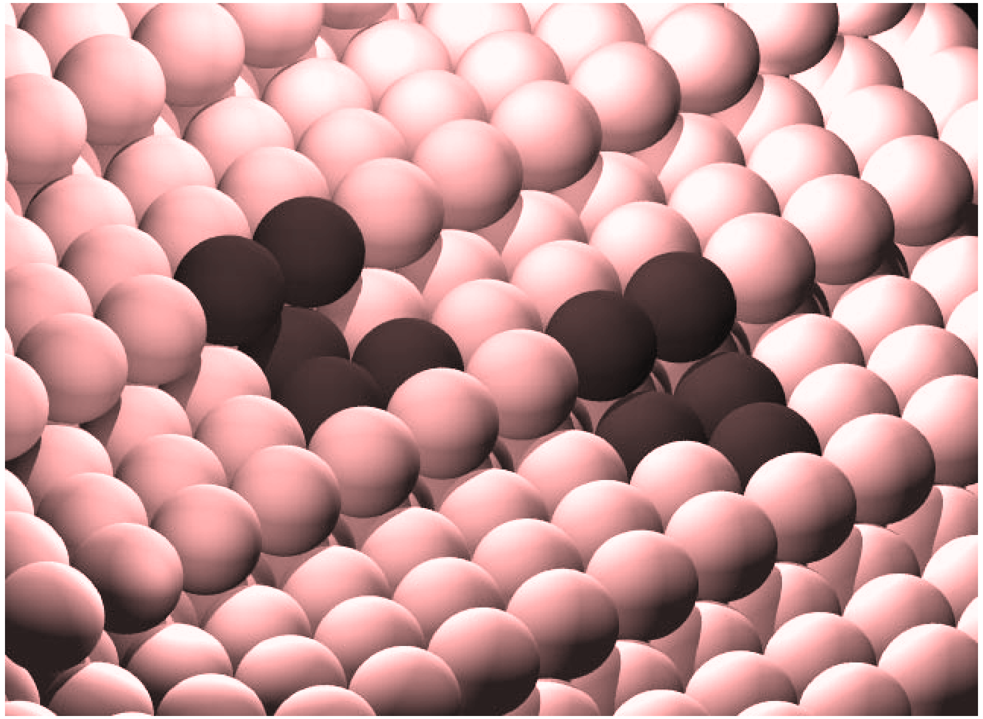


Fig. 3. Ansicht der Einrichtung für Gaszufuhr am Siemens-Übermikroskop.

Holy Grail: Can we Observe an Active Catalyst/Nanoparticle?

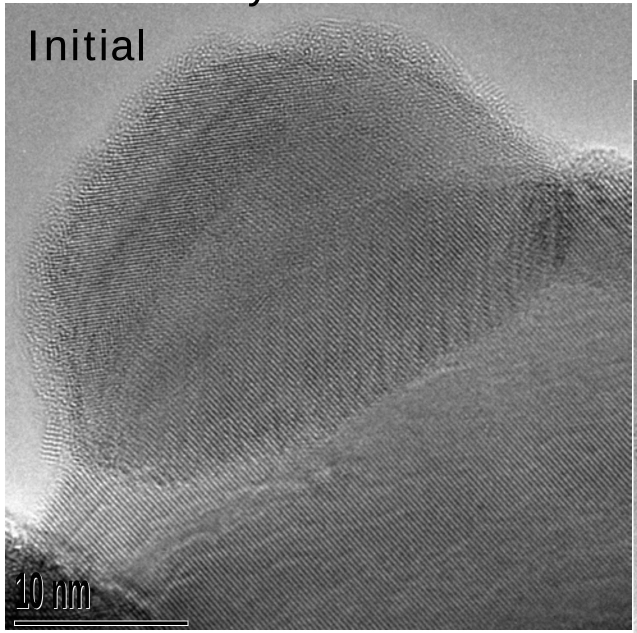


b_5 sites on the (105) surface of Ru. These sites were proposed to be the active sites for N_2 splitting (van Hardeveld and von Montfoort Surf. Sci 4 (1966) 396. Figure from T.W. Hansen *et al.* Catal. Lett. 84 (2002) 7.

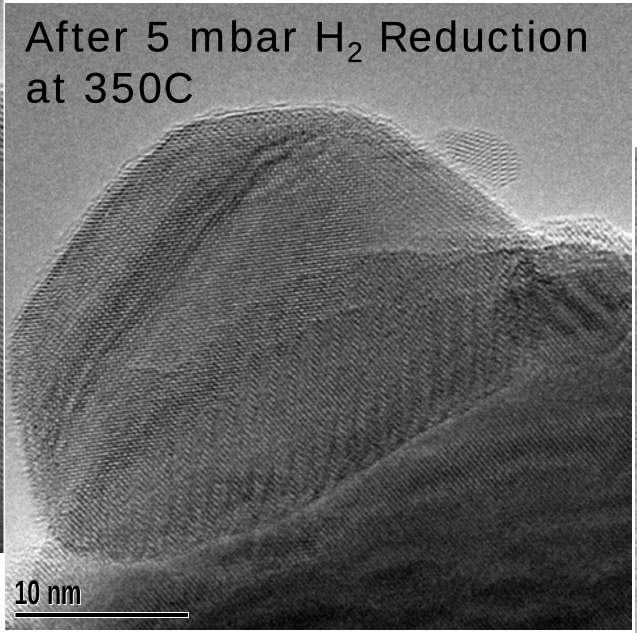
- Materials respond **dynamically to changes in environment**
  - Phase transitions
  - Surfaces are different in vacuum vs. gaseous atmospheres
  - Surfaces reconstruct due to gas adsorption/desorption
  - Growth
  - **Dynamics**
- Conventional electron microscopy does not always tell the full story
  - Samples are (usually) not in their operational environment -> **sites are normally not active in vacuum**

Stages of a catalysts Life
- PdZn/ZnO for Methanol Steam Reforming

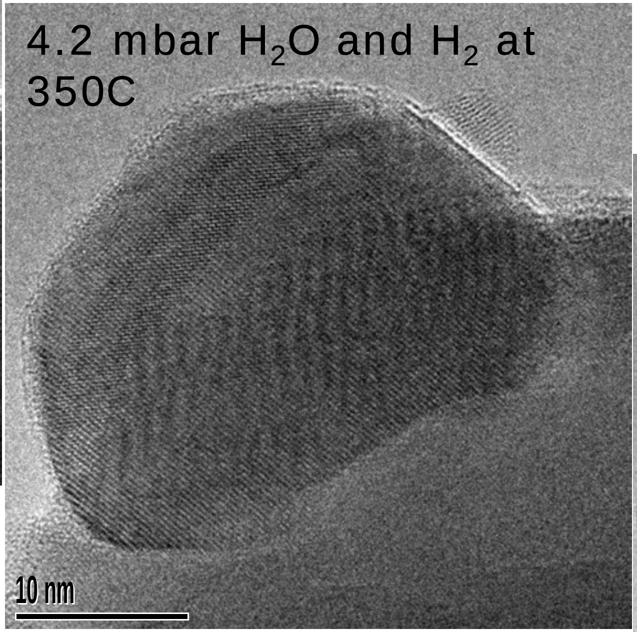
“As synthesized”



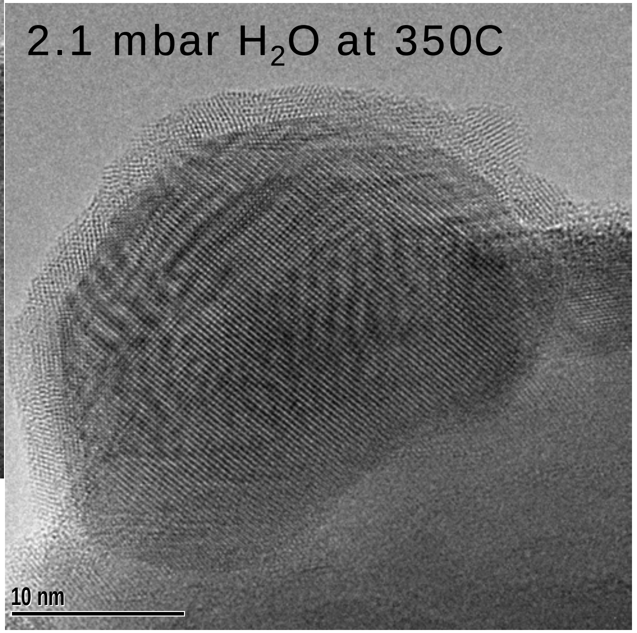
“Activation”



“Reaction”



“Deactivation”



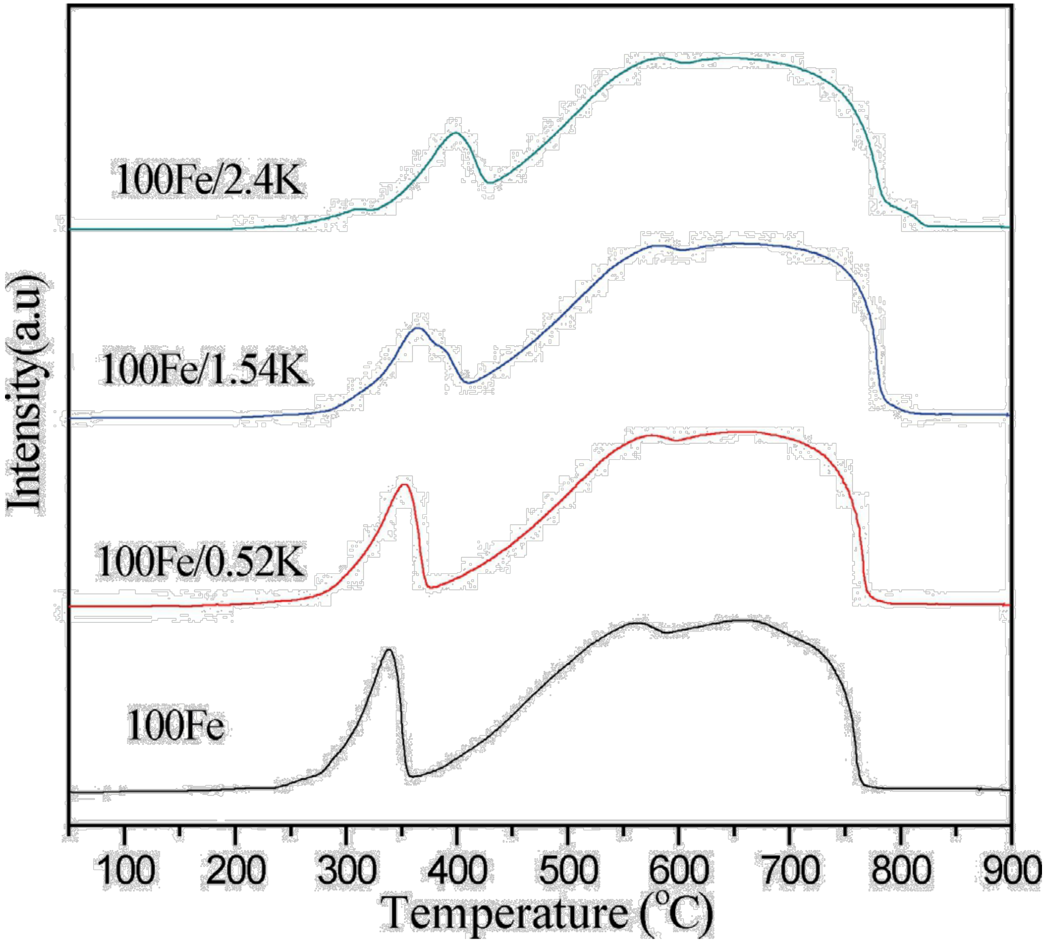
C. Carillo, A. Datye. J.B. Wagner and T.W. Hansen, unpublished

Motivation

Iron Oxide

- **Fischer-Tropsch Synthesis**
- Iron oxide is a precursor for iron carbide based Fischer-Tropsch synthesis catalysts.
- Looking at **global** and **local** information with both **in situ XRD** and **TEM**.
- Covering a **vide pressure range**, ranging from **mbar** (ETEM) to **bar** (Climate).
- The **active phase** can be achieved by **reducing hematite** (α-Fe_2O_3) to Magnetite (Fe_3O_4) and in some cases completely to metallic iron (α-Fe).

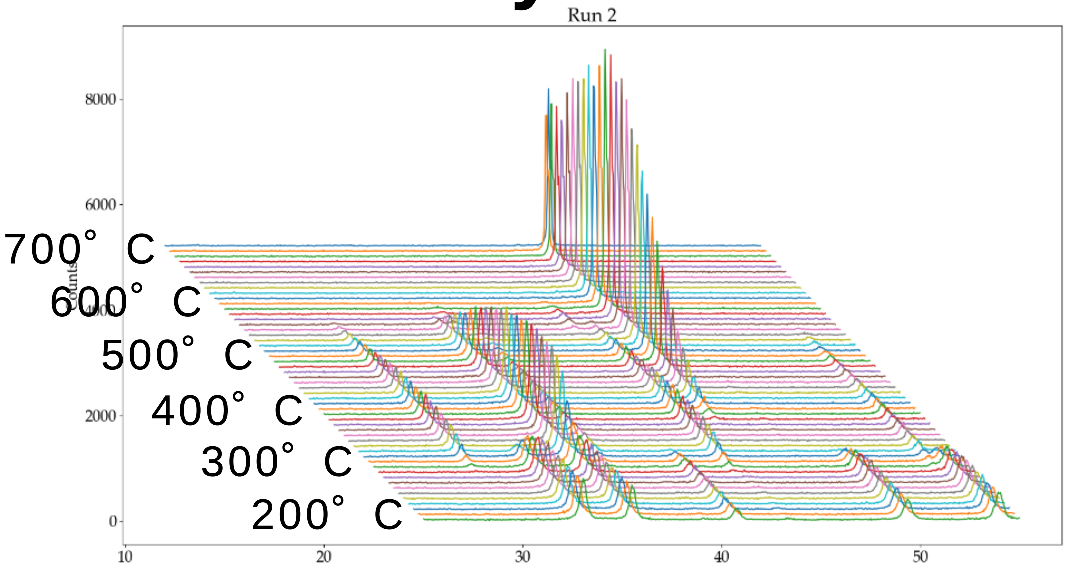
H_2-TPR

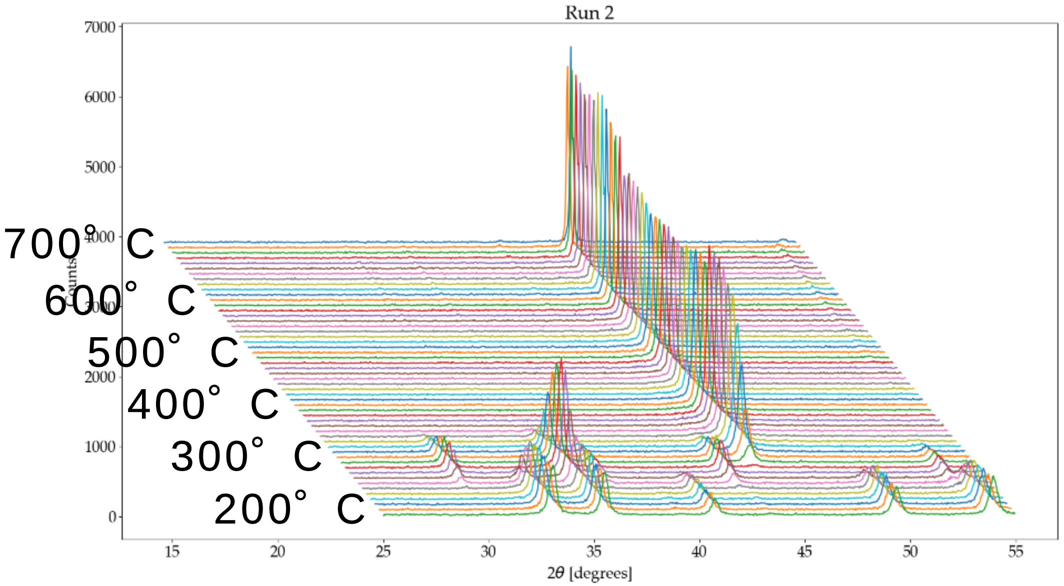


Niu, L et. al. ChemCatChem 9 (2017) 1691-1700

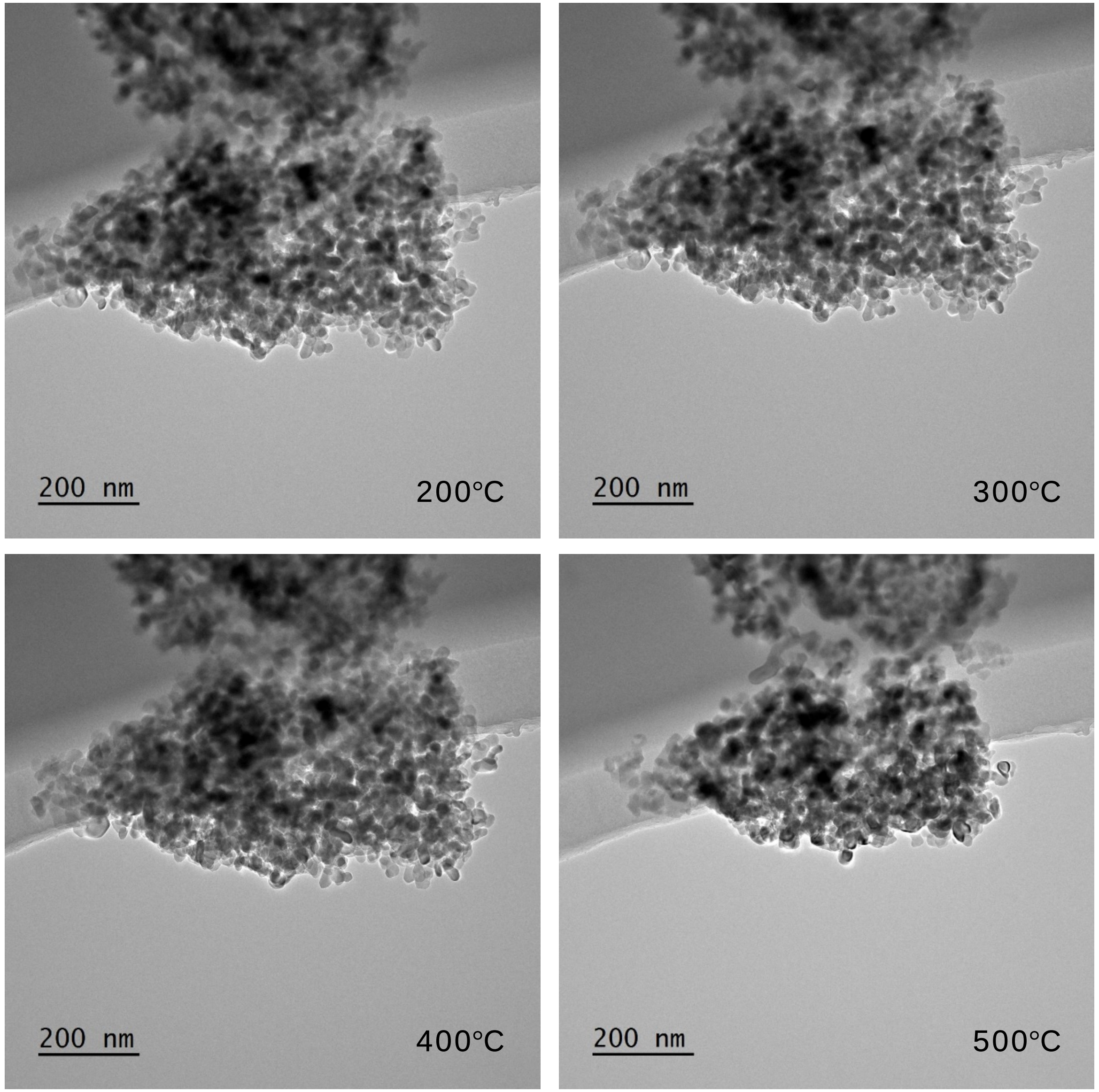
Reduction vs. H_2 Pressure Monitored by *in situ* XRD

- Temperature ramp: 40°C/h
- Flow: 2/100 nml/min
- Pressure: 20/1000 mbar
- Conversion to both Fe_3O_4 and Fe starts at lower temperatures
- We would expect similar observations in Wildfire/Climate holders





Reduction in ETEM



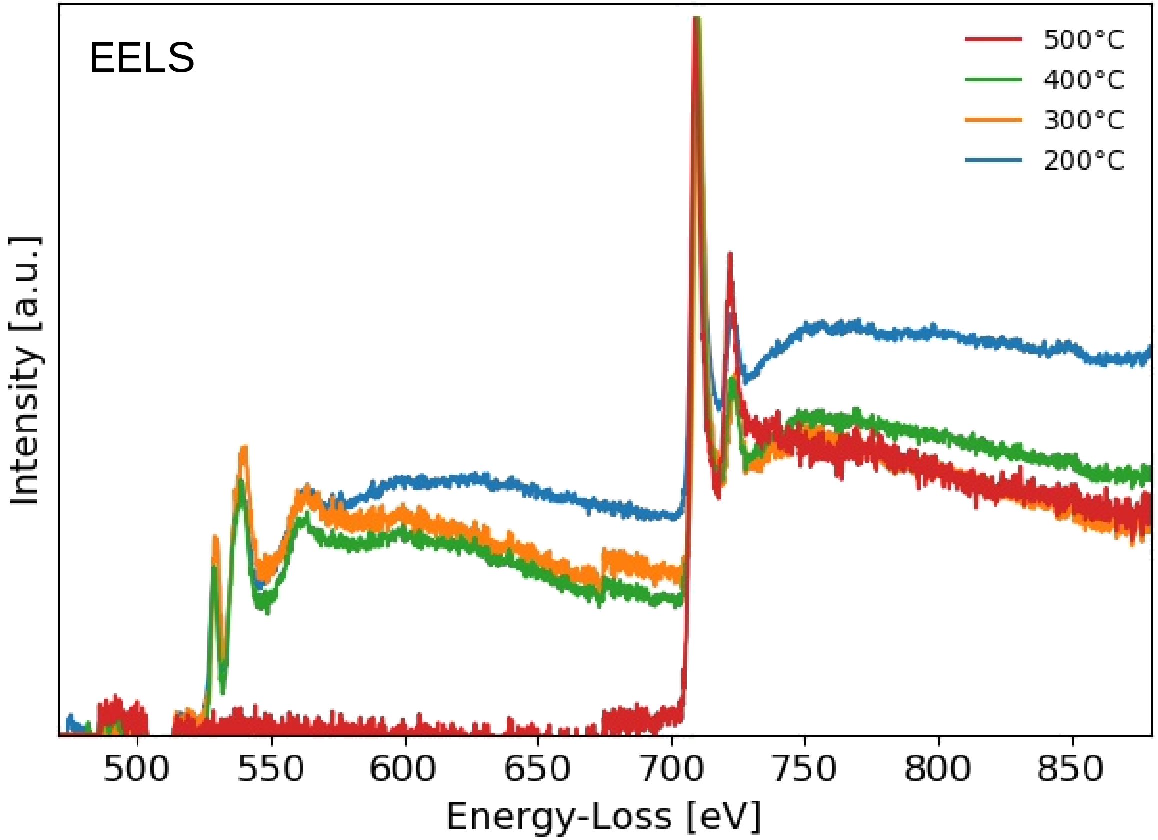
H_2-reduction of α-Fe_2O_3

Pressure: 1.3 mbar

H_2-flow: 2 ml/min

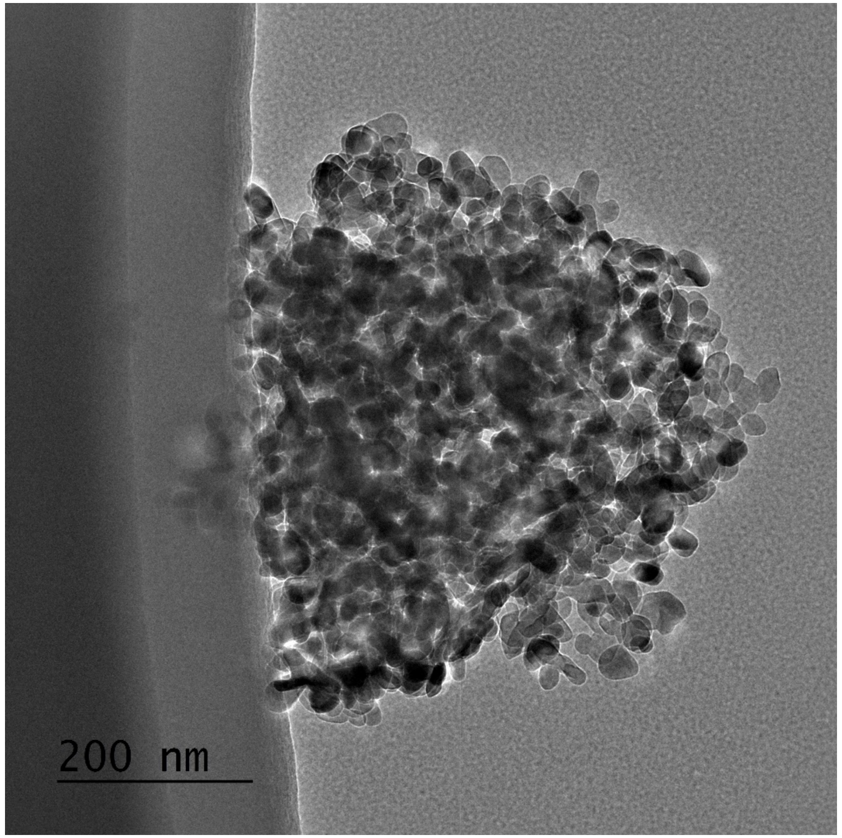
Dose rate: $4.6 \cdot 10^3$ e^-/nm^2

Particles remain small



Reduction in Climate

H_2-reduction of α-Fe_2O_3



Temperature: 150°C

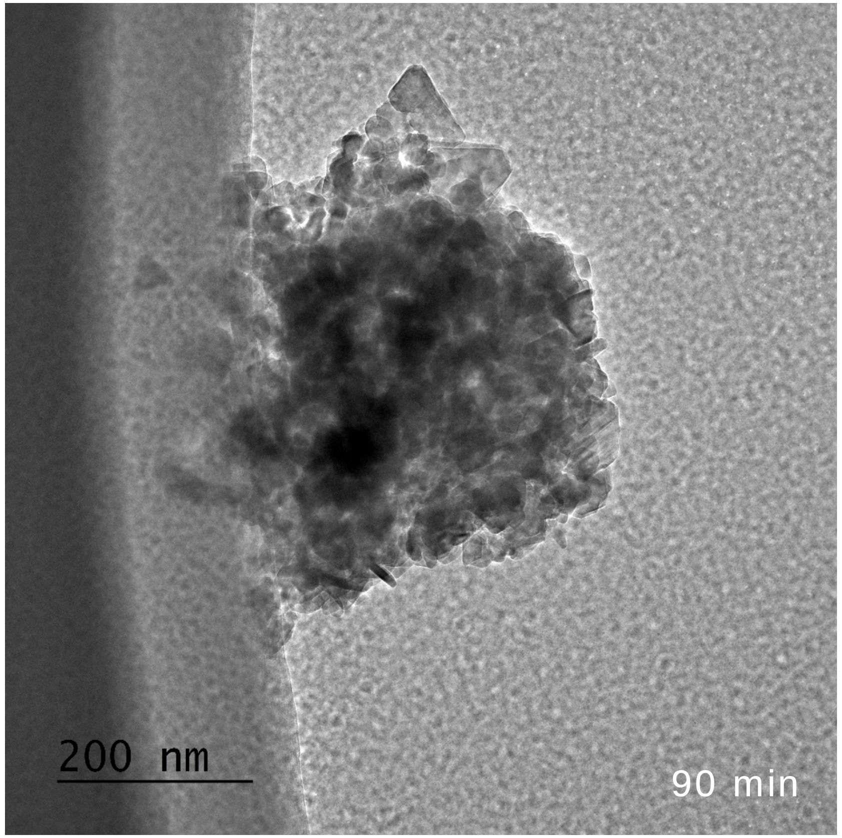
Dose rate: $2.6 \cdot 10^3$ e^-/nm^2

Temperature: 700°C

H_2-flow: ~0.9 ml/min

Pressure: ~950 mbar

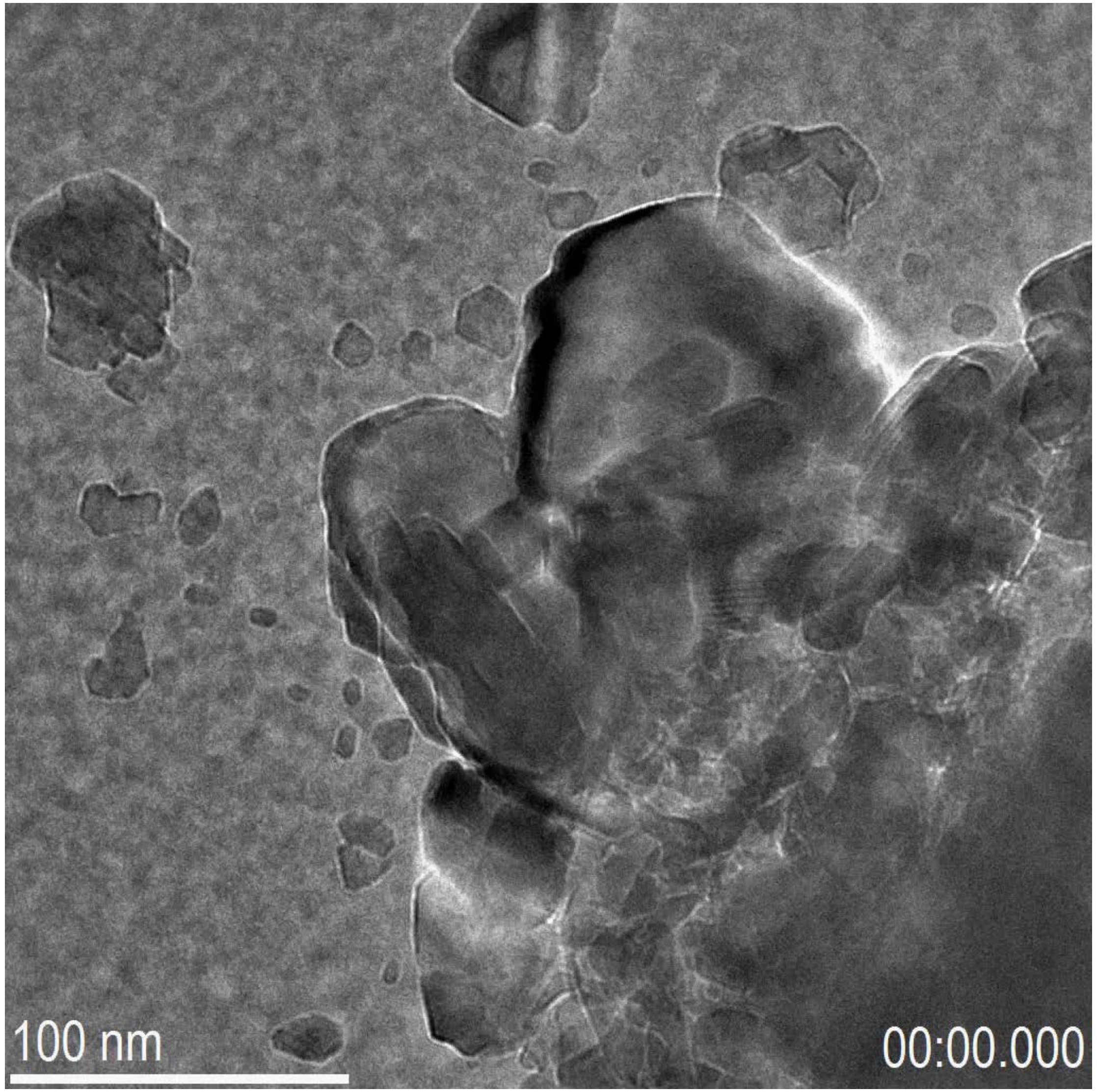
Dose rate: $5.6 \cdot 10^3$ e^-/nm^2



Reduction of Fe_2O_3 in Climate

- 0.8 ml/H_2
- Temperature: 800°C
- P(in): 700 mbar
- P(out): 500 mbar
- P(nr): ~ 610 mbar
- Flow ~0.6 ml/min

- Densification of sample
- Competing reactions, could be oxidation fighting reduction



Reduction of Fe_2O_3 in Climate

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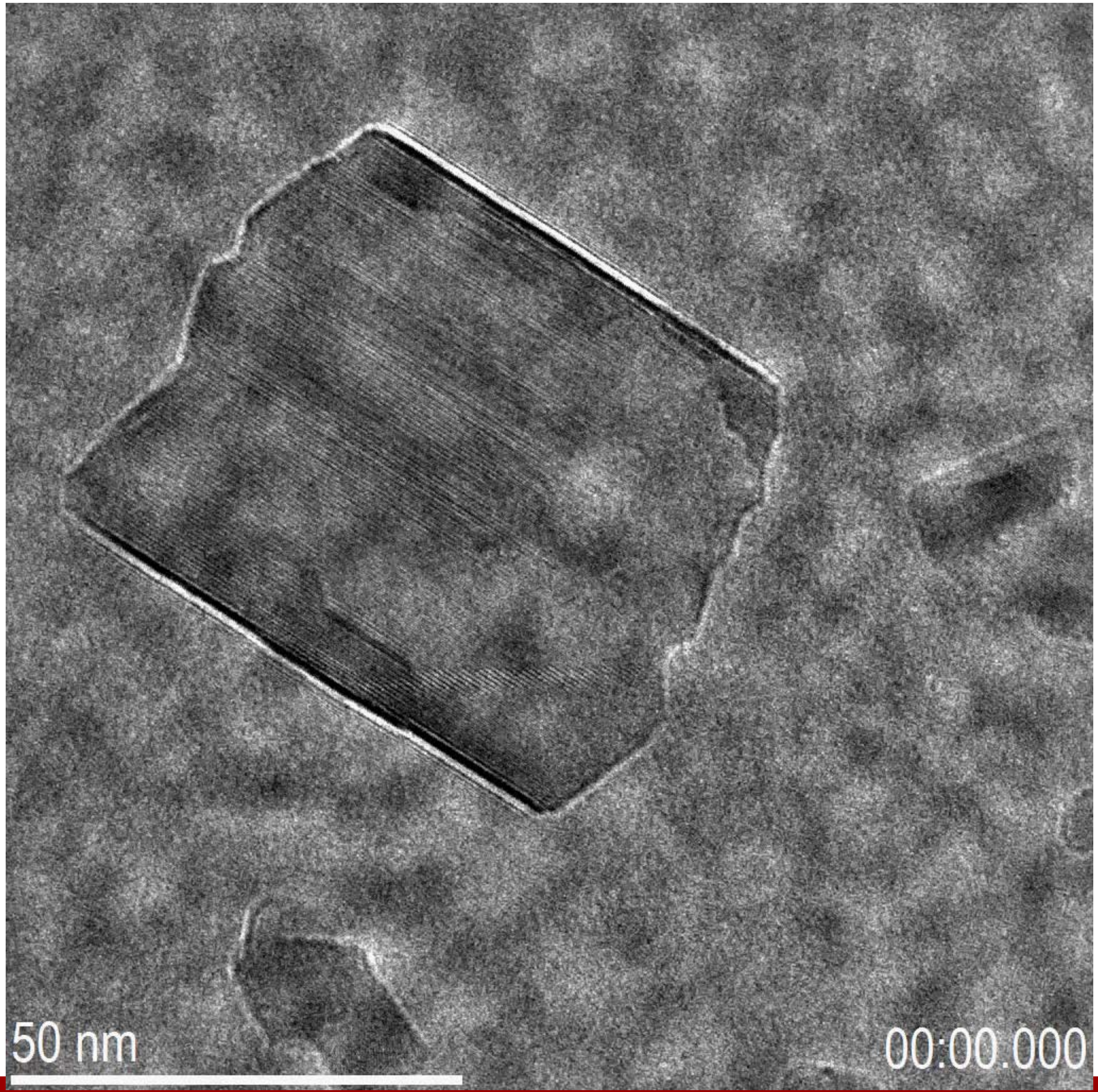
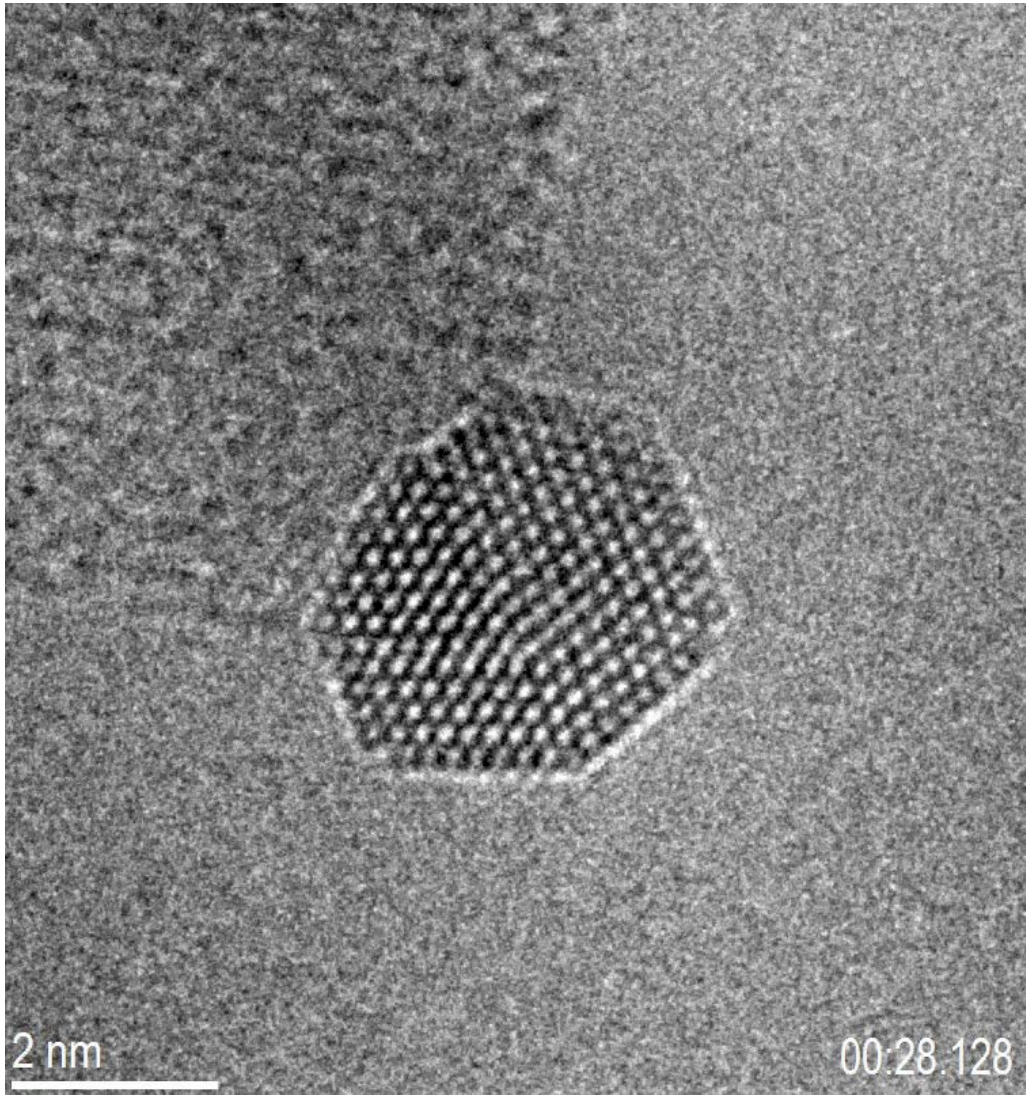
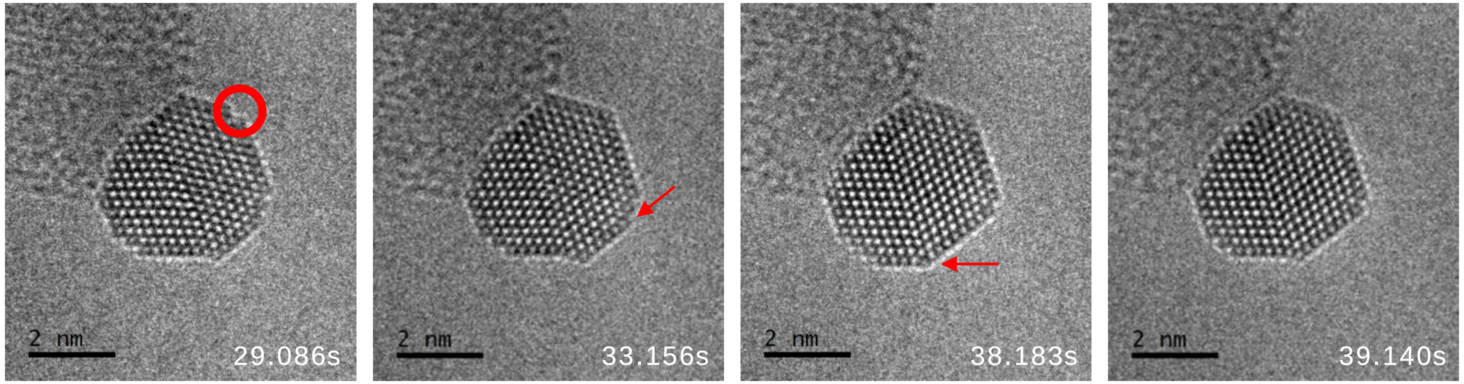


Surface Activity on Rh Particles Supported on TiO_2





3wt% Rh/TiO_2 reduction

Climate holder

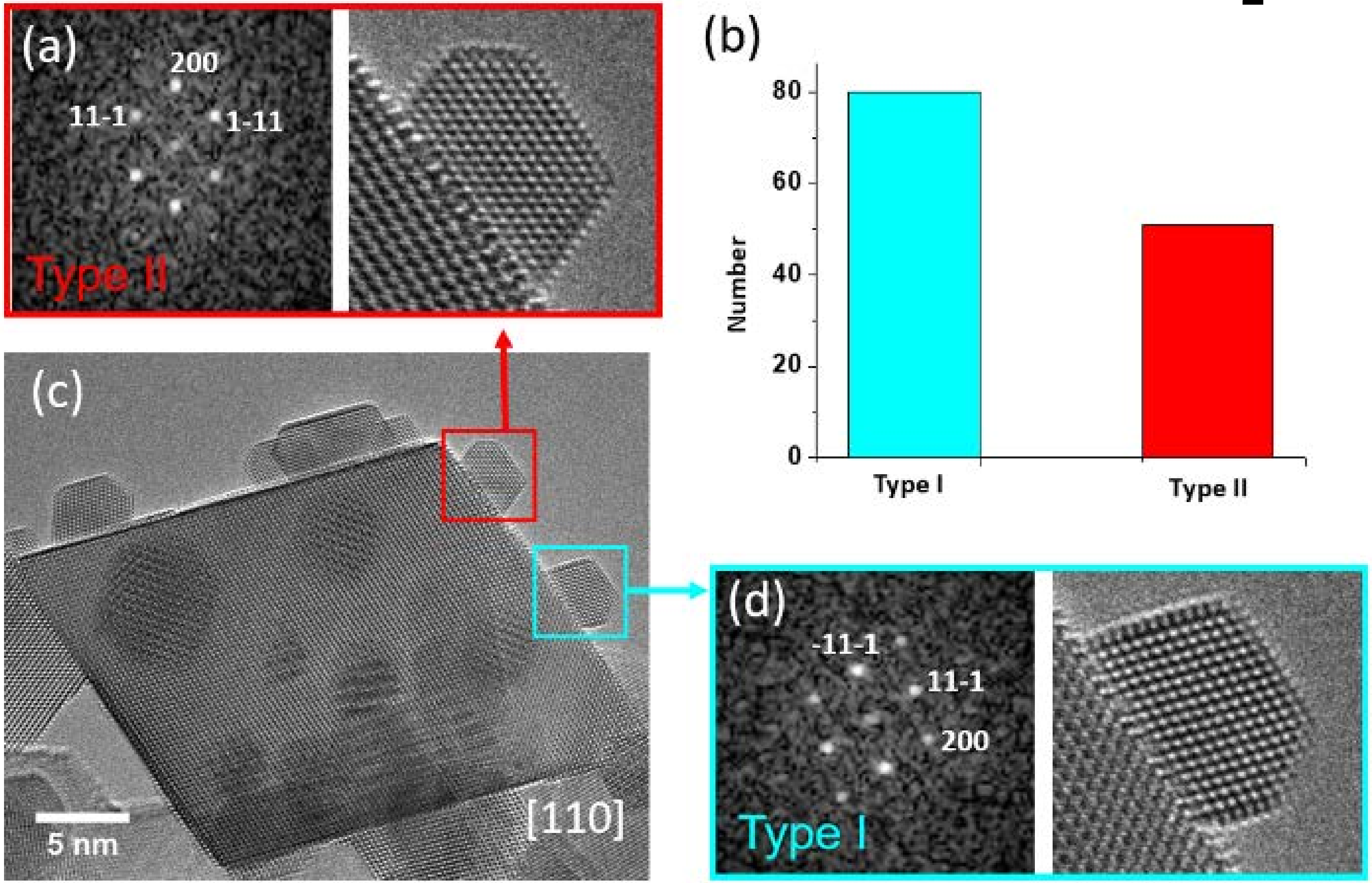
Temperature: 400°C

H_2-flow: 0.9 ml/min

Pressure: 900 mbar

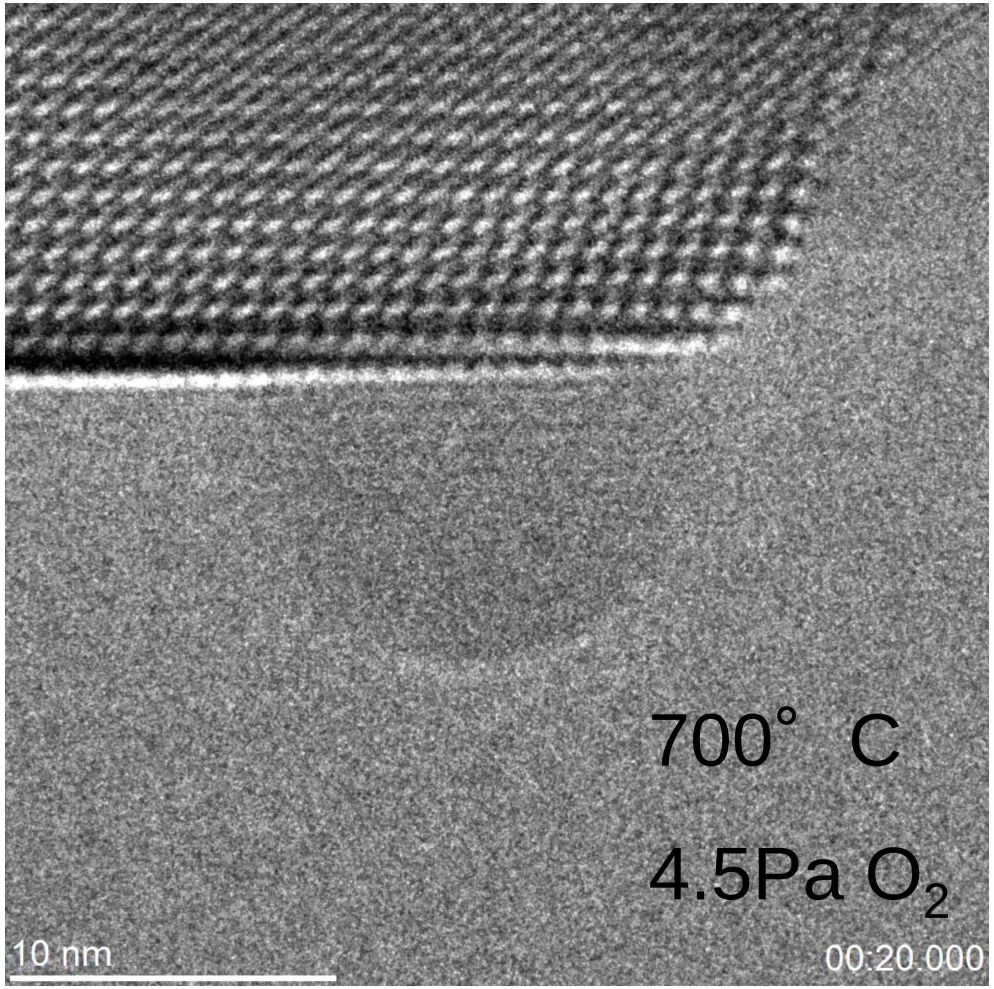
Dose: $7.6 \cdot 10^5$ e^-/nm^2

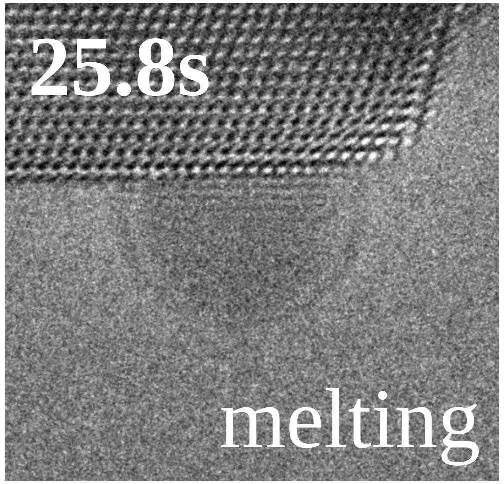
Transformations of Au Particles on CeO_2

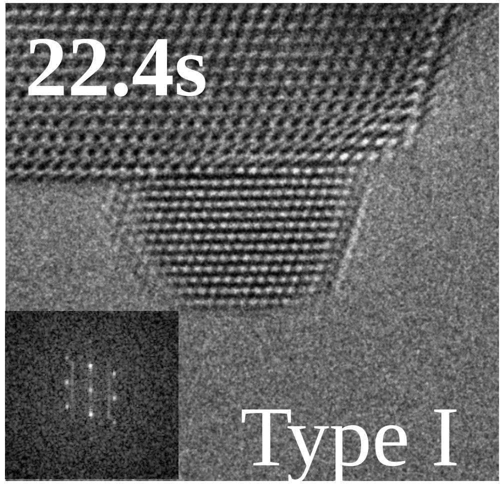


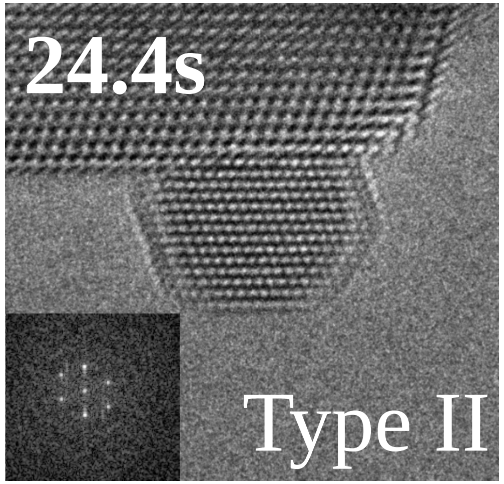
P. Liu, TWH, *et al.*, Nanoscale (2019) Accepted

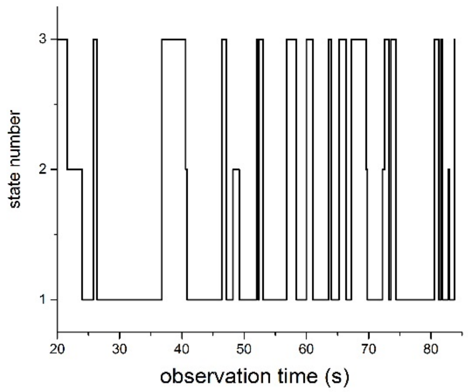
Au/CeO_2 Configurations





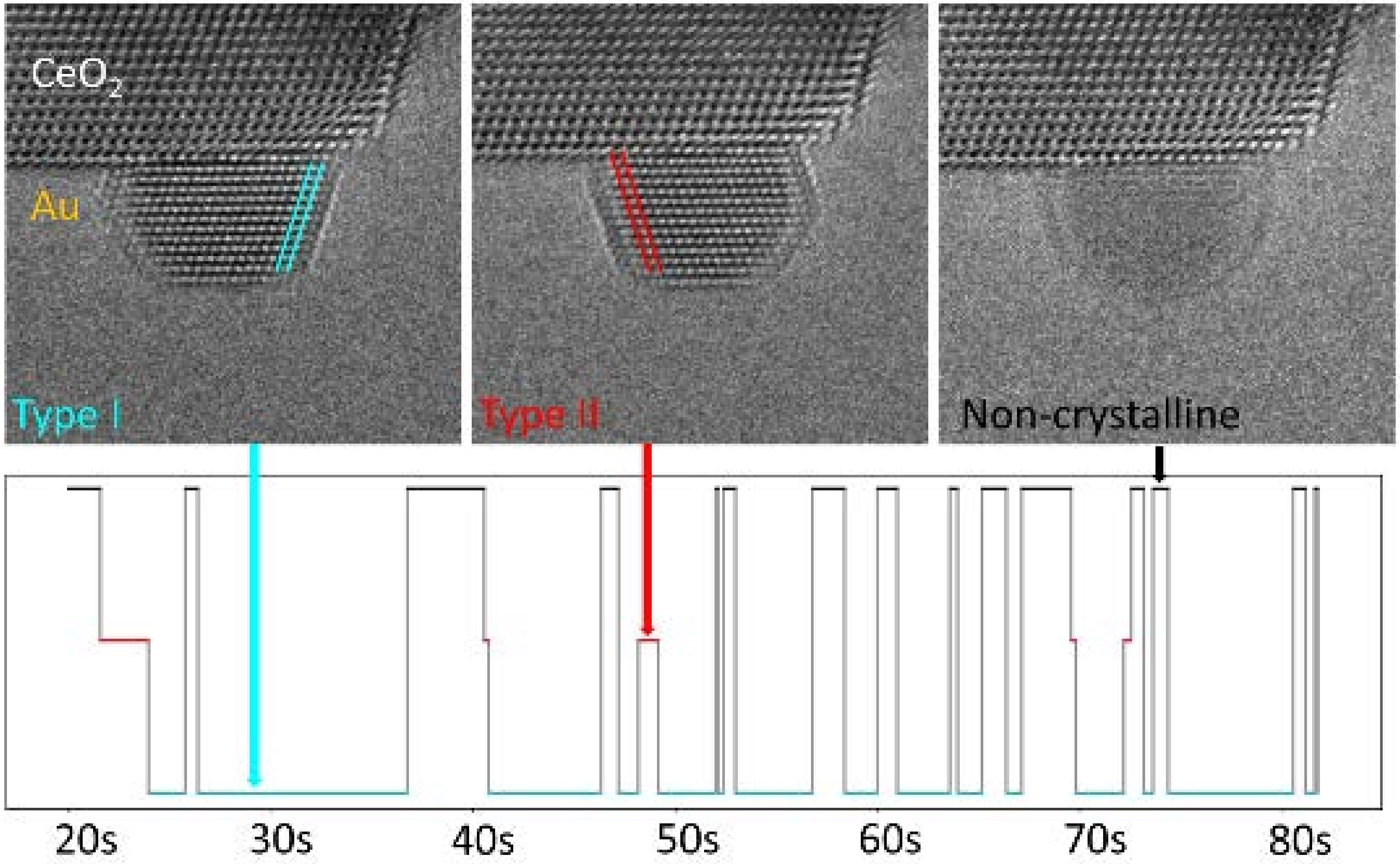






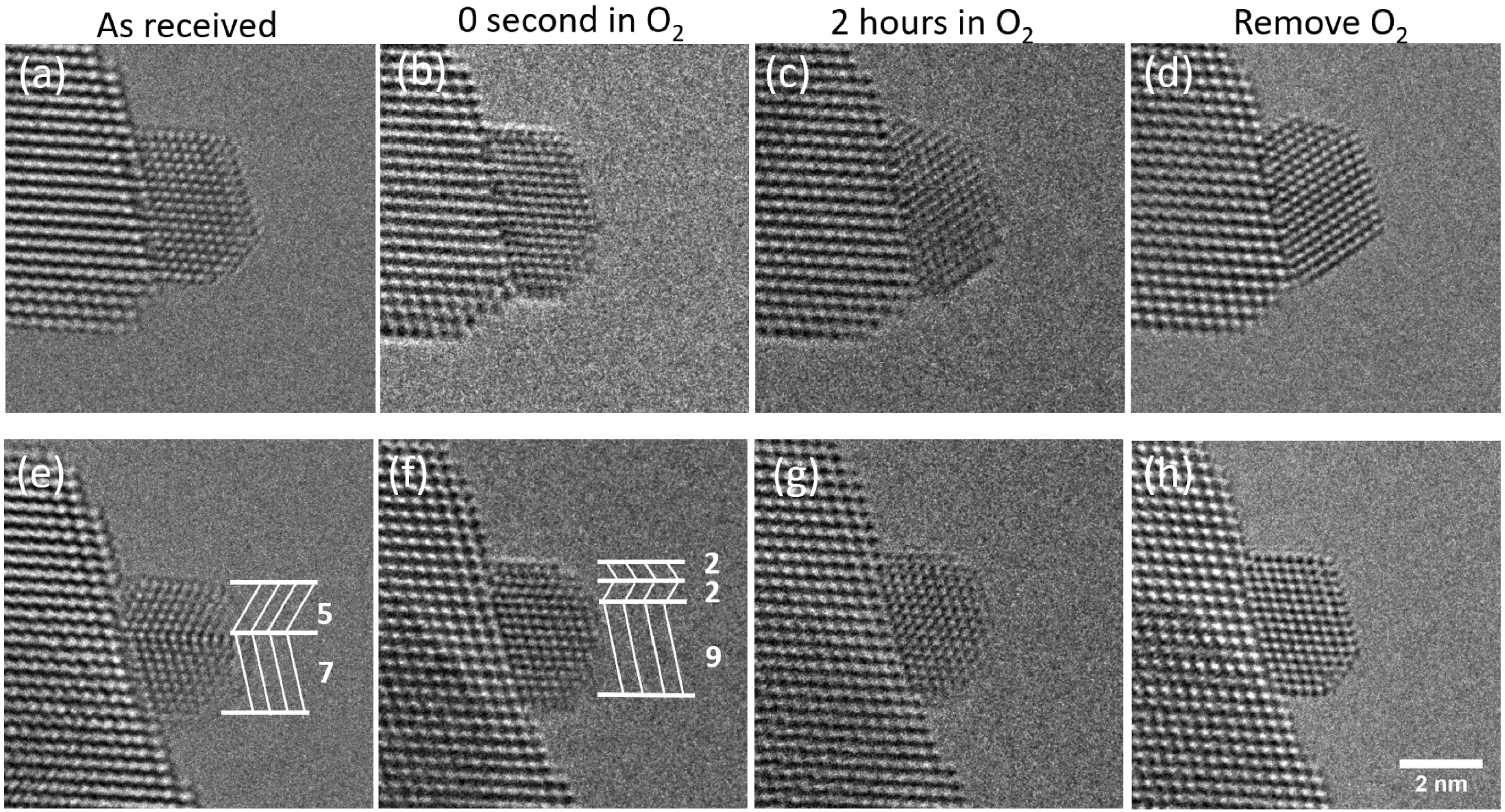
P. Liu, TWH, *et al.*, Nanoscale (2019) Accepted

Quantifying the States



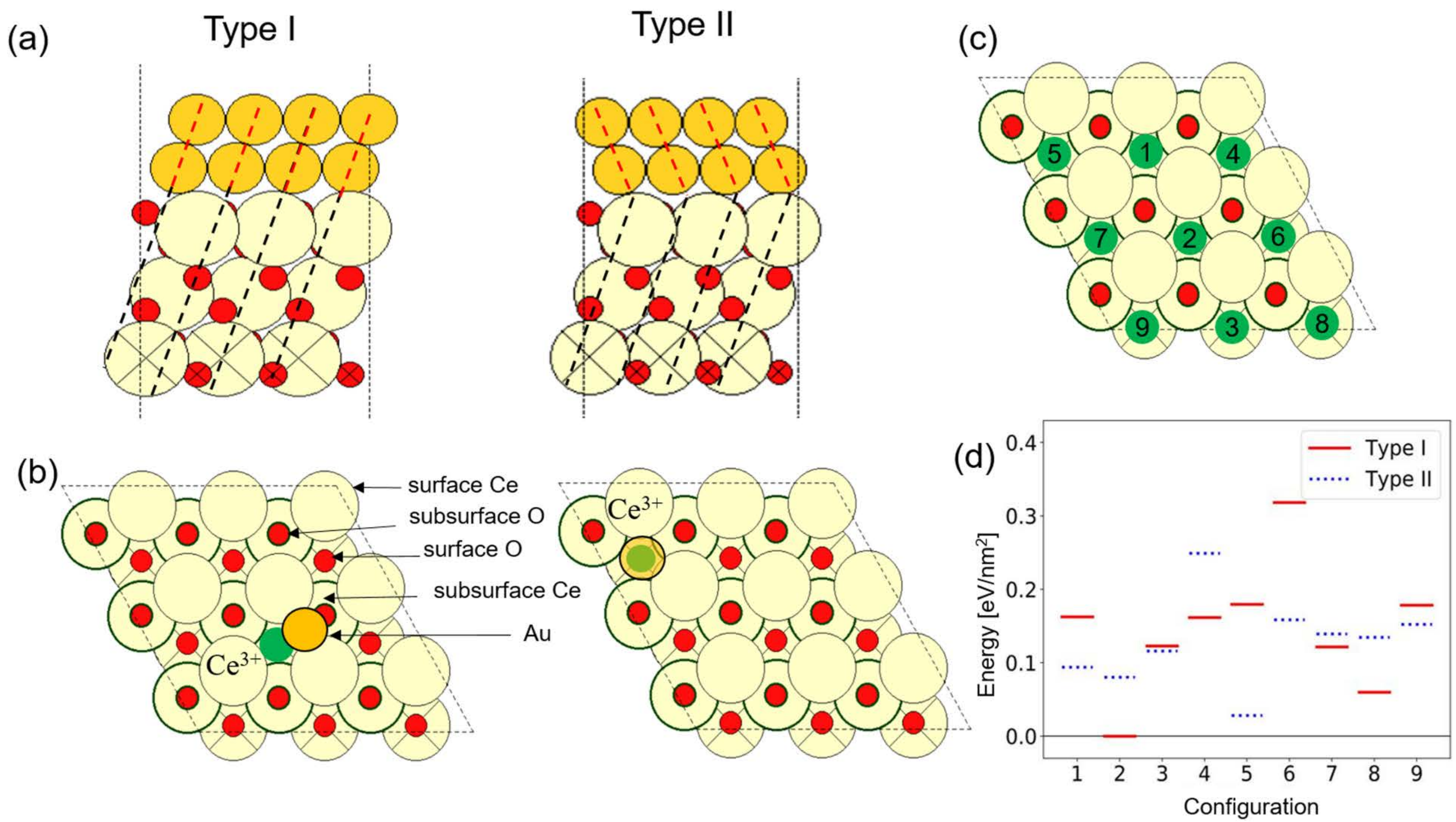
P. Liu, TWH, *et al.*, Nanoscale (2019) Accepted

Transformations of Au Particles on CeO_2



P. Liu, TWH, *et al.*, Nanoscale (2019) Accepted

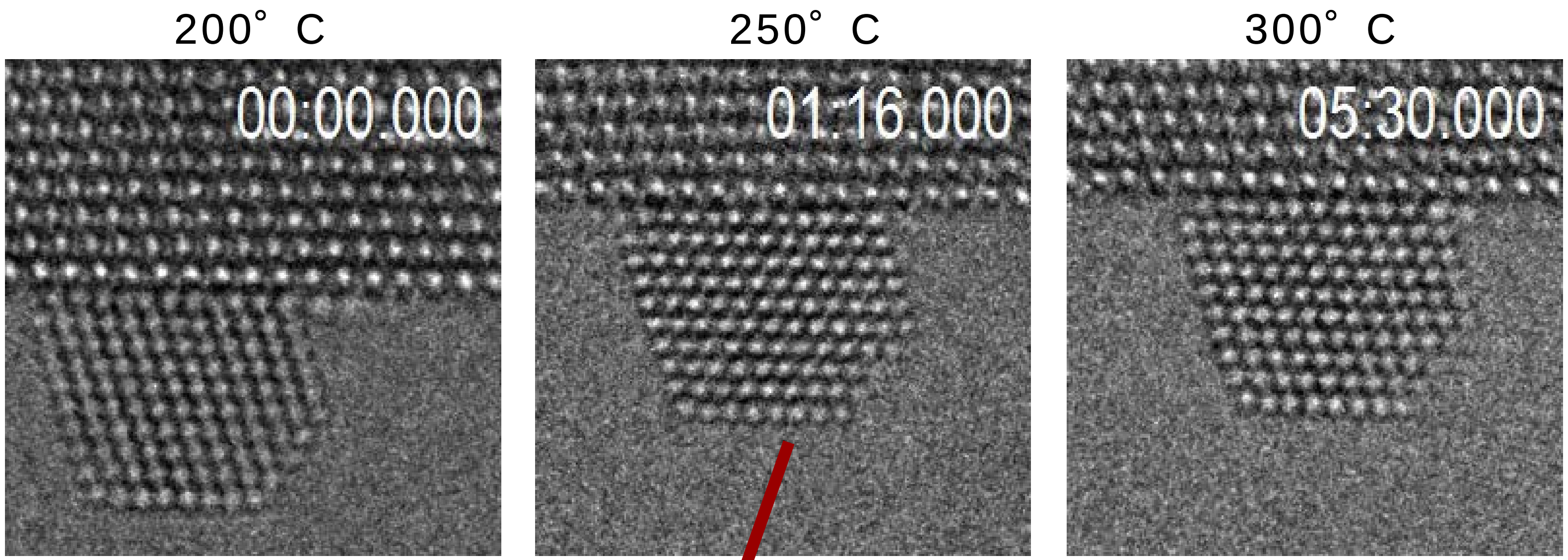
Energy levels vs. Vacancy Configuration

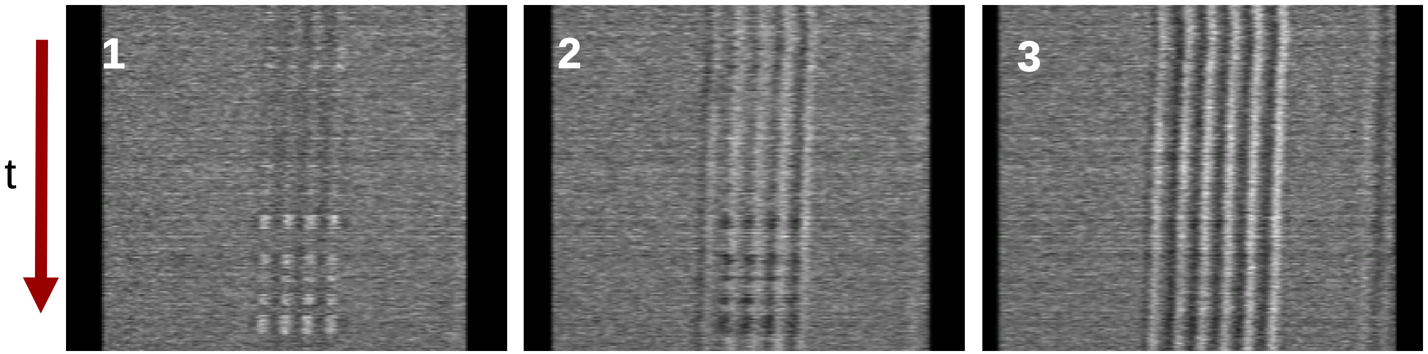


P. Liu, TWH, *et al.*, Nanoscale (2019) Accepted

COMPUTATIONAL ANALYSIS APPROACHES

Surface Restructuring - Au/CeO_2 4.5 Pa CO





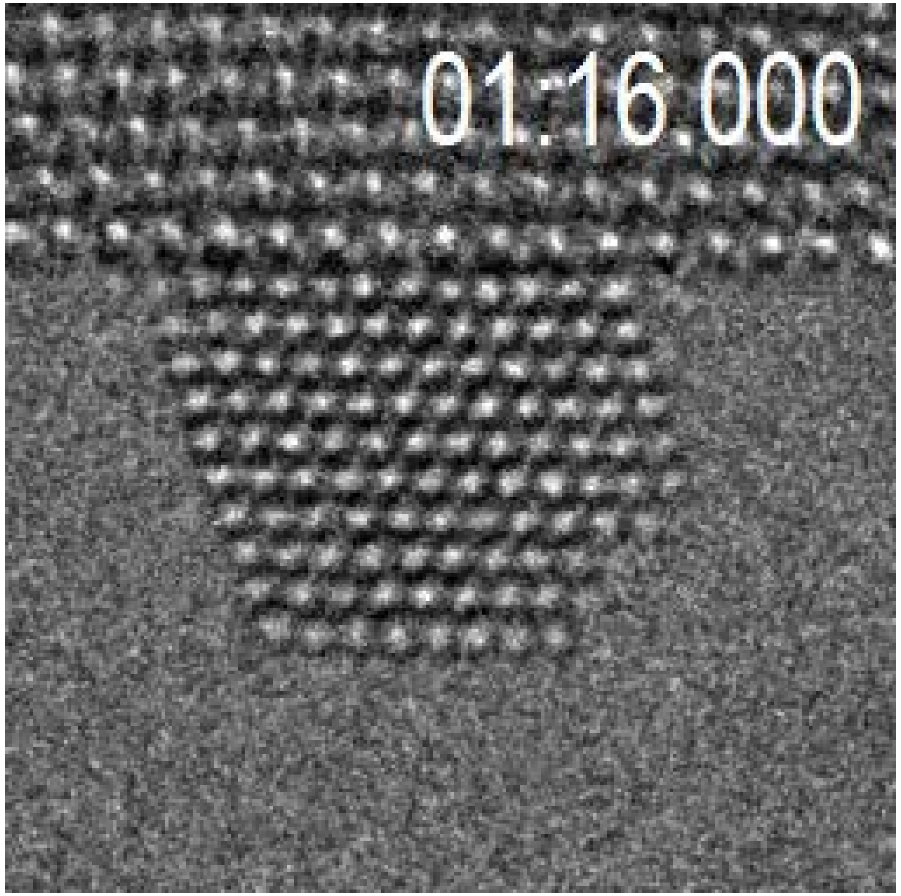
Topmost three layers of the (100) facet @250° C

- As the temperature is increased, different surface phenomena are excited
- At 200° C, surface atoms are barely dynamic
- At 250° C, entire layers shift
- At 300° C, The entire surface becomes dynamic and columns on all facets shift in a concerted motion

J. Madsen, TWH, *et al.*, Adv. Theory Simul., 1800037 (2018)

J. Madsen, TWH, *et al.*, Adv. Struct. Chem. Imag., 3, 14 (2017)

Motivation: Large amounts of data
- Image sequences, high frame rates…



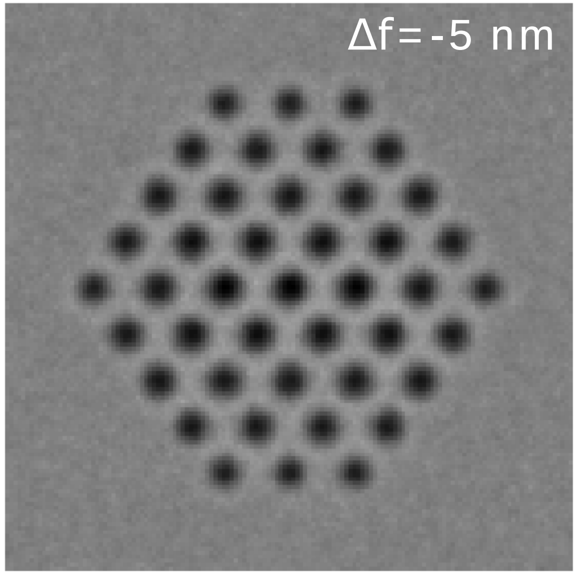
Gold on CeO_2 substrate.

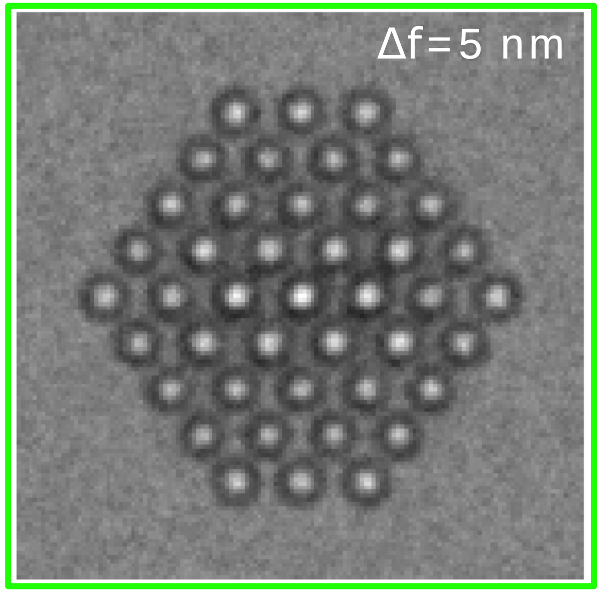
4.5 Pa CO @250° C

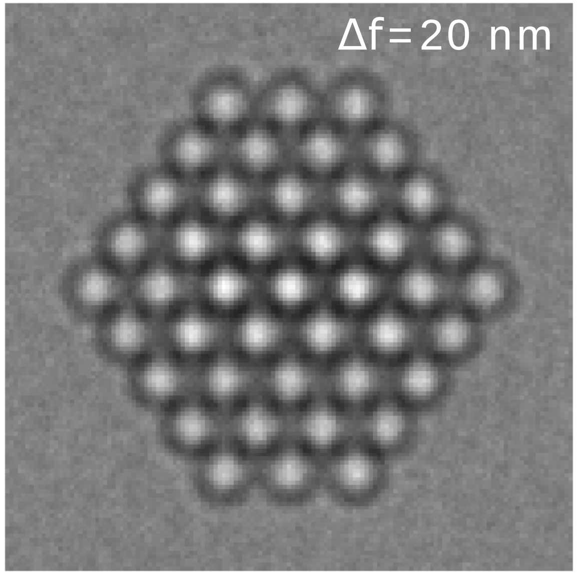
- Image-corrected 300 keV FEI Titan ETEM, Gatan OneView@0.2 frames/sec

- Huge and boring undertaking to log the positions of all atoms at all times. Especially as frame rate and temporal resolution goes up

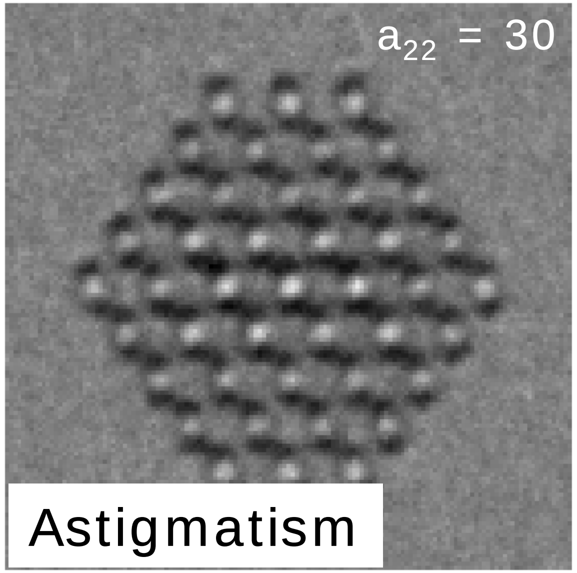
Analyzing HRTEM images is not just peak finding!



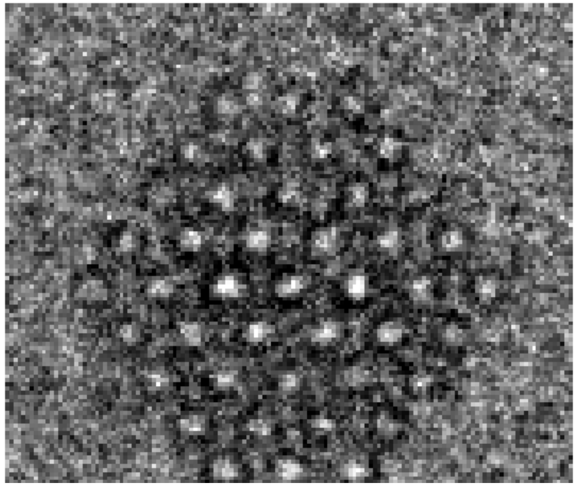




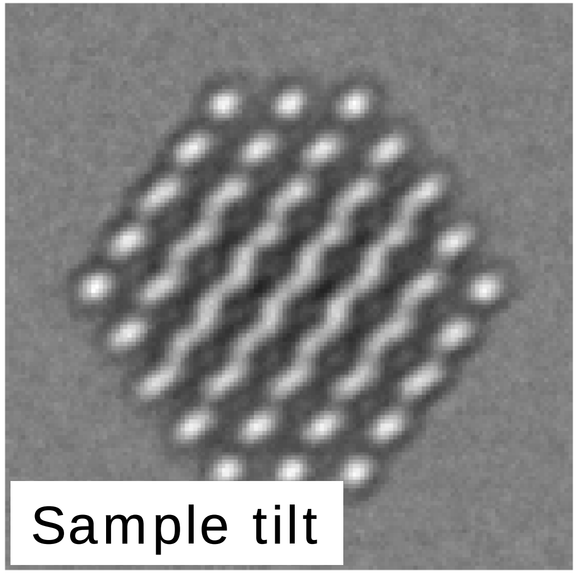
Defocus, height difference and contrast inversion



Astigmatism

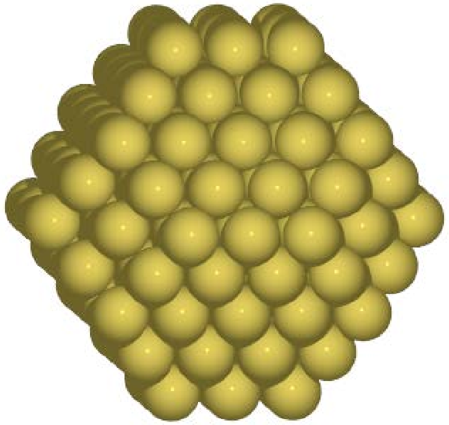


Low dose/high noise

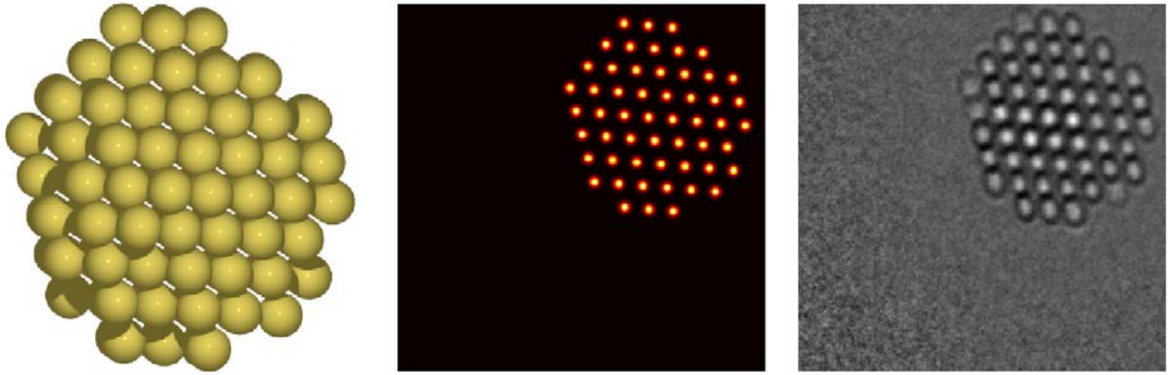


Sample tilt

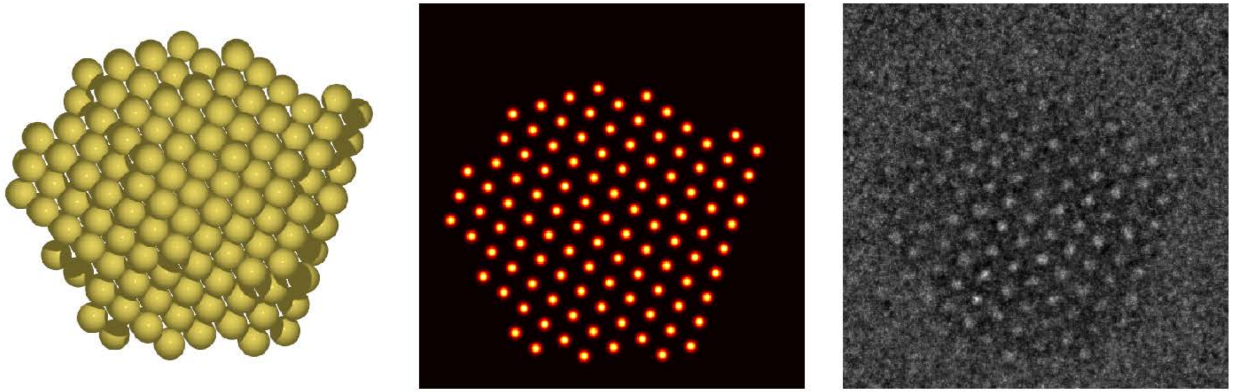
All images on this slide are simulated with PyQSTEM

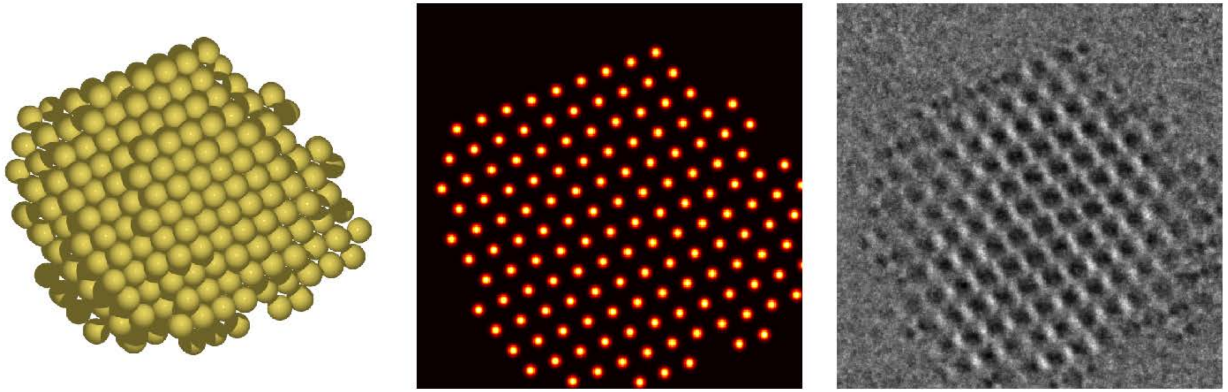


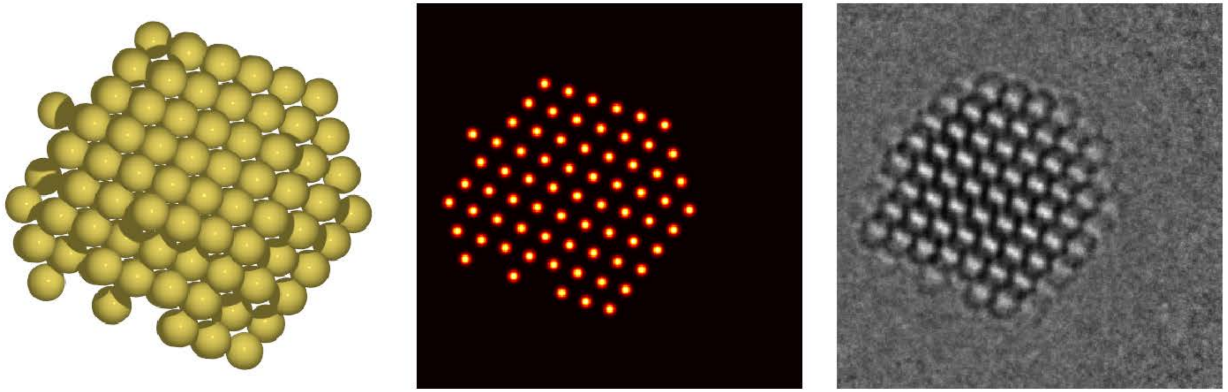
Training the network



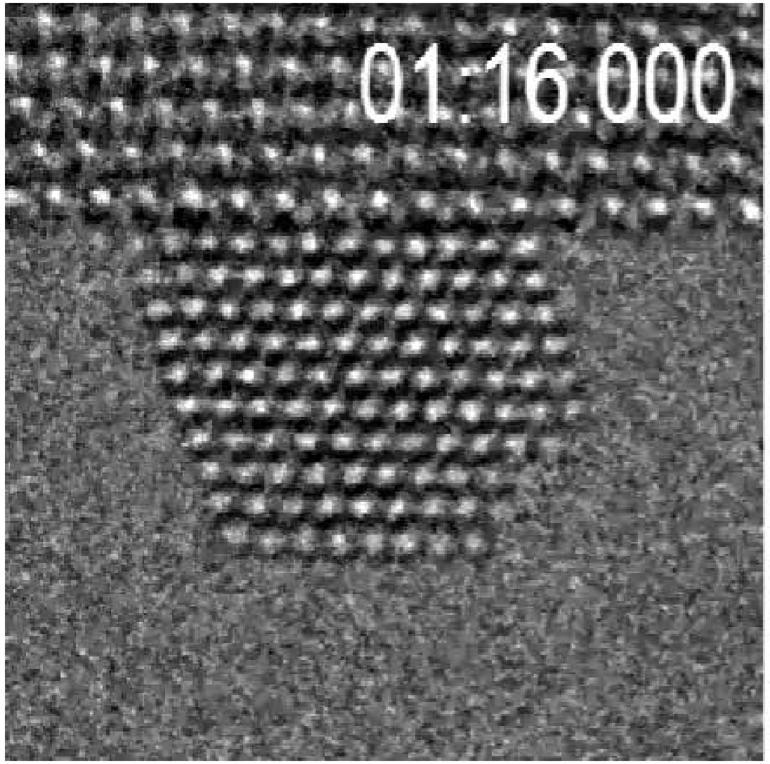
- Training a neural network requires **many** well-labeled examples
  - Typically expensive / hard to produce
- **We can generate simulated HRTEM images for training!**
  - Inexpensive and easy
  - We use PyQSTEM, a Python interface to the QSTEM program by Christoph Koch

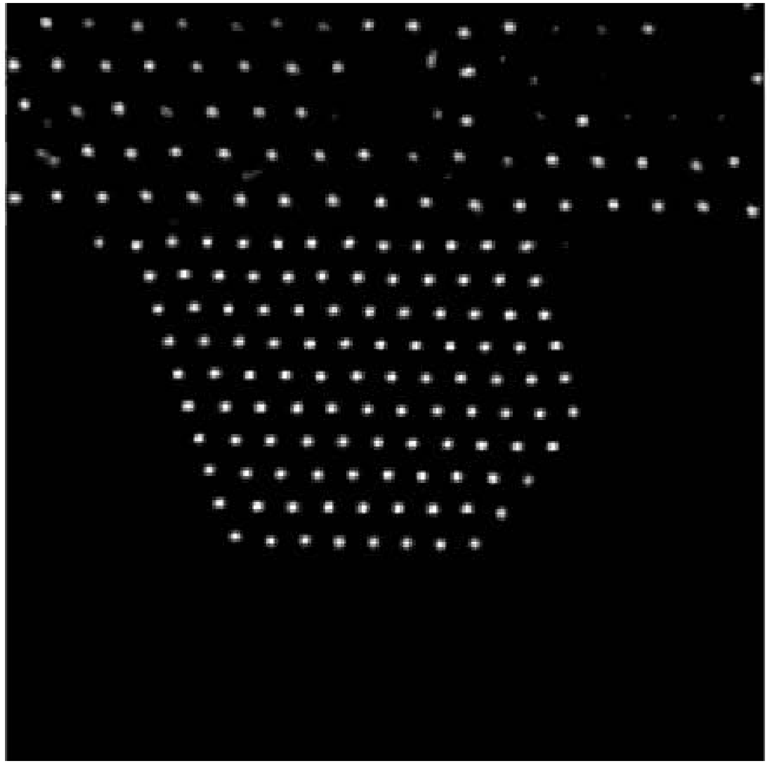


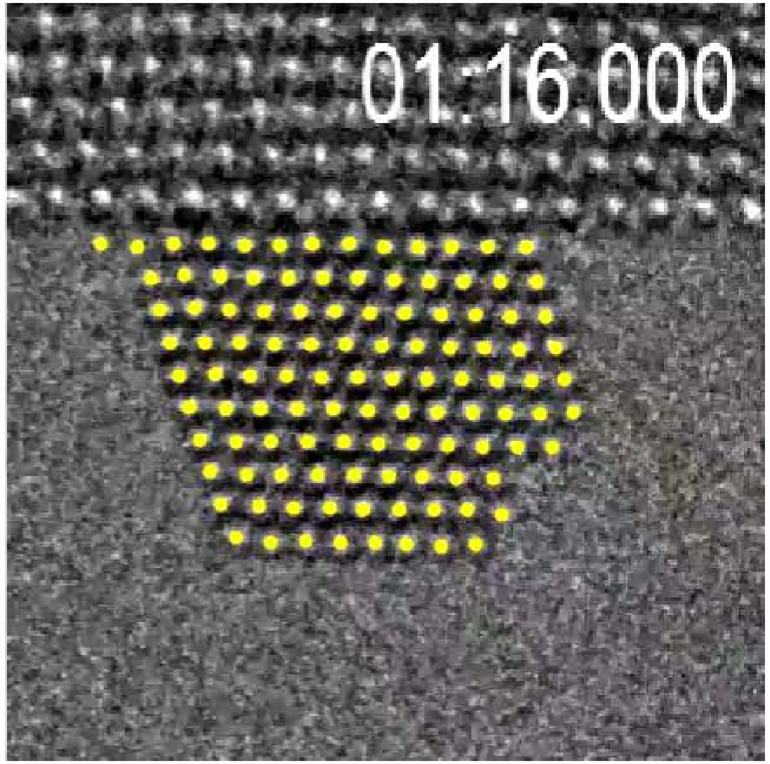




Results: Gold Nanoparticle on Ceria

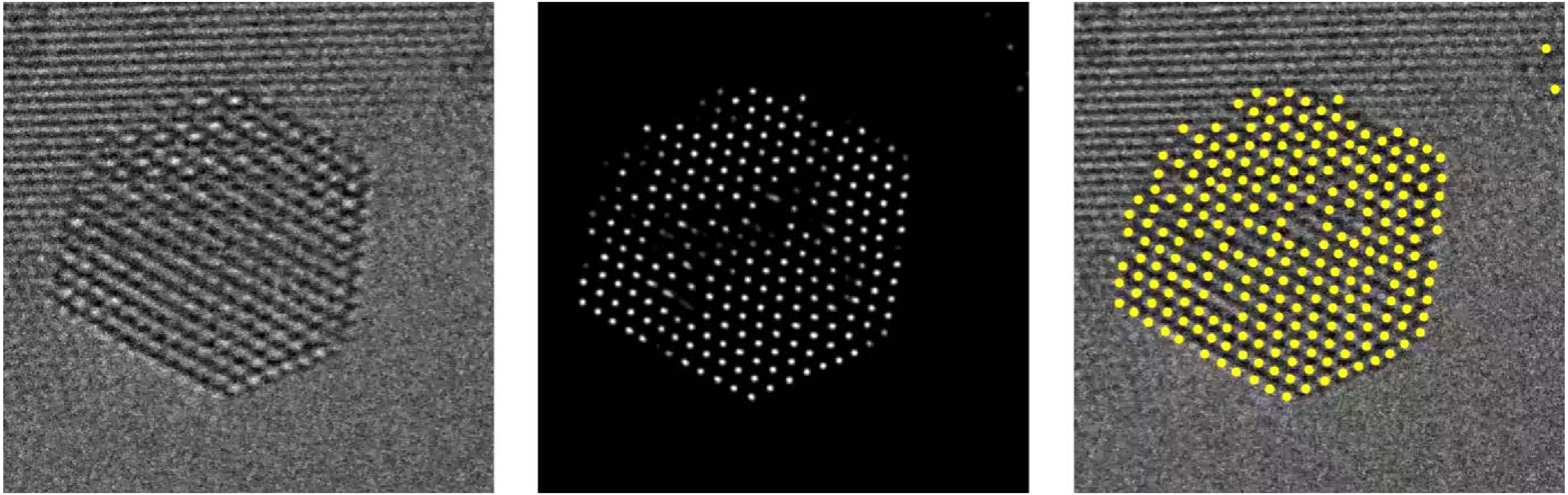






- Concerted diffusion
- Image-corrected 300 keV FEI Titan ETEM (4.5 Pa CO@250°C).

Results: Gold Nanoparticle on Ceria



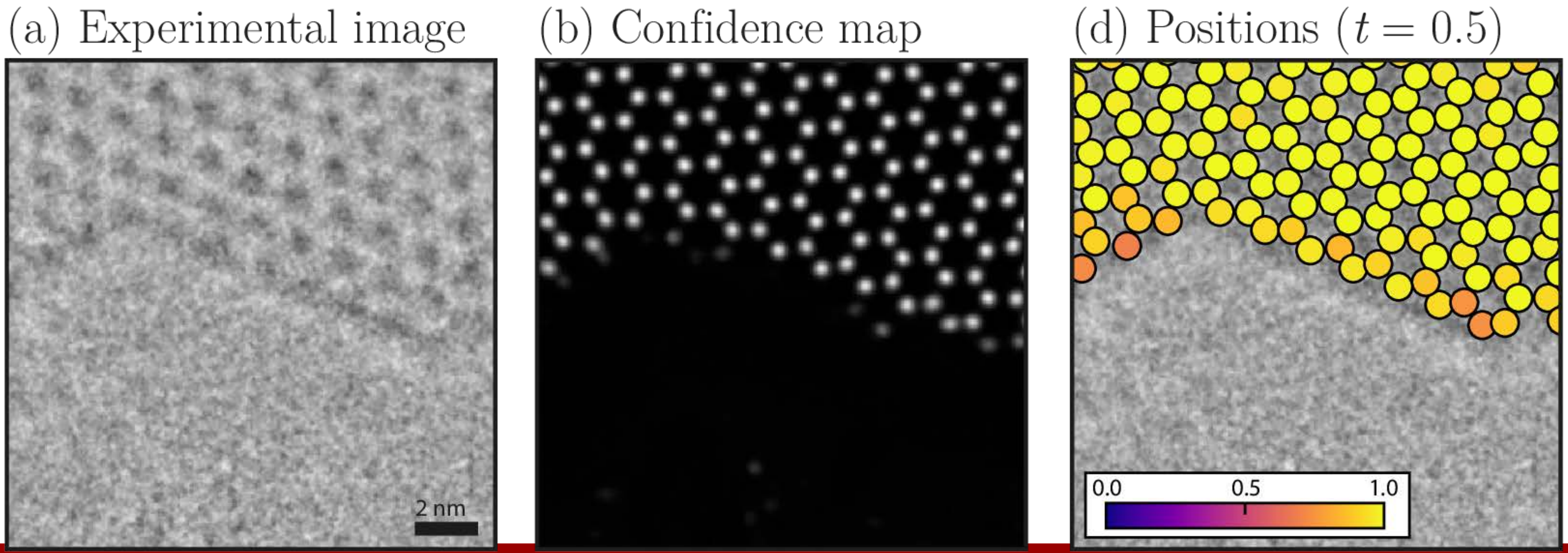
Au/CeO_2 in vacuum

Surface buckling

Results: Graphene

l (b) Simulated image: $I(\boldsymbol{x})$ (c) Ground truth: $P(\boldsymbol{x})$ (d) Prediction: $\tilde{P}(\boldsymbol{x})$

2 nm



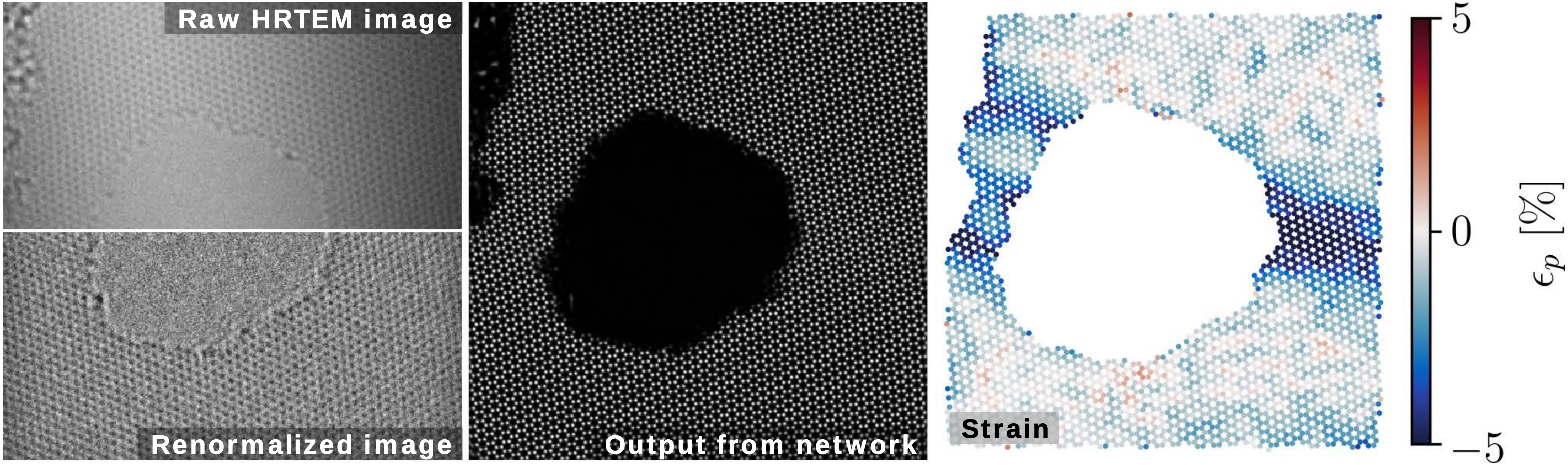
Training data:

Carbon in graphene-like structures.

Regular lattice **NOT** in training set!

Application to an experimental image.

Results: Graphene



Strain in beam-damaged graphene calculated from the atomic positions found by the neural network.

J. Madsen, TWH, *et al*, Adv. Theory Simul., 1800037 (2018)

J. Madsen, TWH, *et al.*, Adv. Struct. Chem. Imag., 3, 14 (2017)

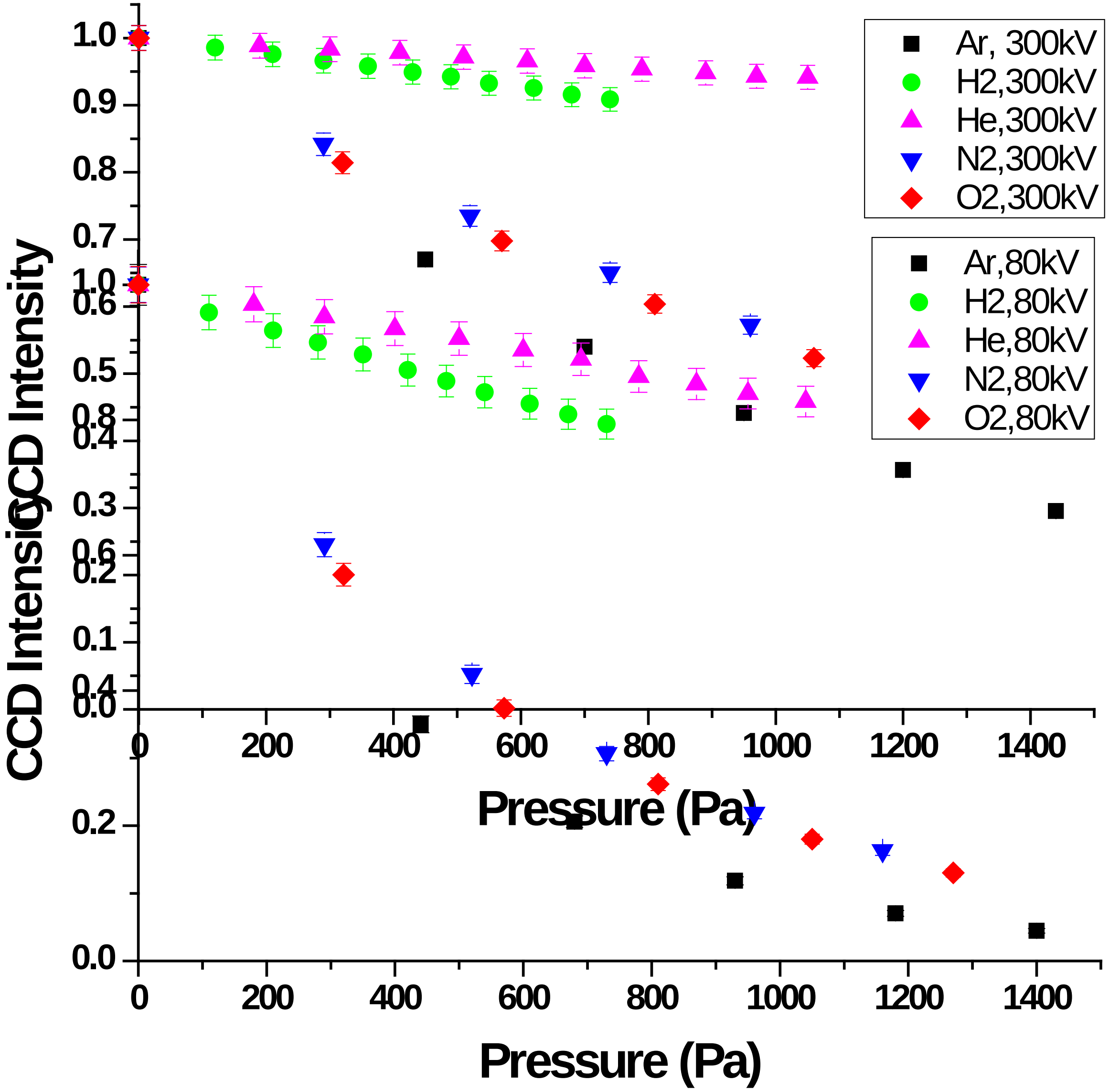
TOWARDS UNDERSTANDING THE ETEM

Imaging in the Fog of Gas

Can we get a clear view...?

Imaging in Gas

- 300kV
- Loss of intensity
- Intensity measured on a bottom mounted camera
- At P>1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2
- 80kV



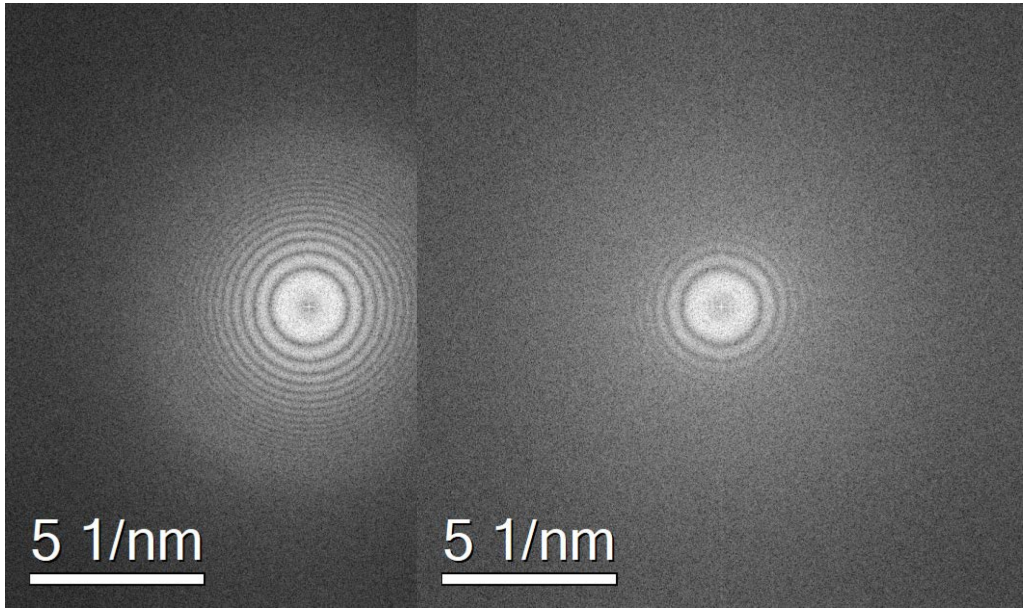
T. W. Hansen *et al. Microsc. Microanal.* 18, 684 (2012)

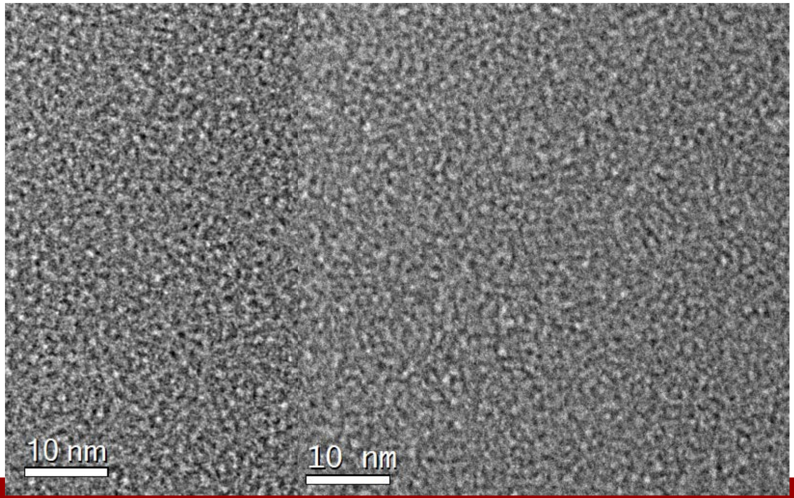
Effects on resolution
-Power spectrum in the presence of gas

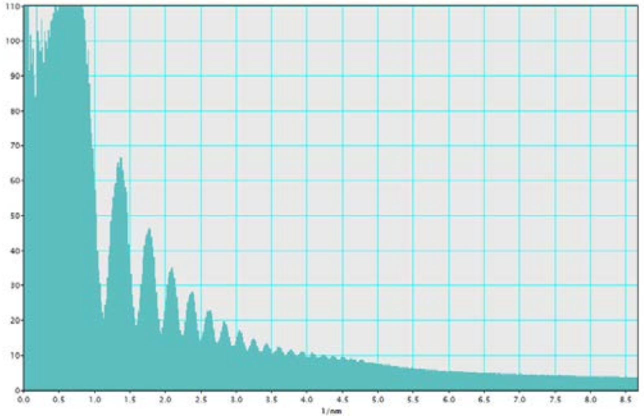
- Effects of gas observed from the power spectrum of amorphous carbon film (imaged at -410nm defocus)

- Vacuum

- 1700 Pa Ar



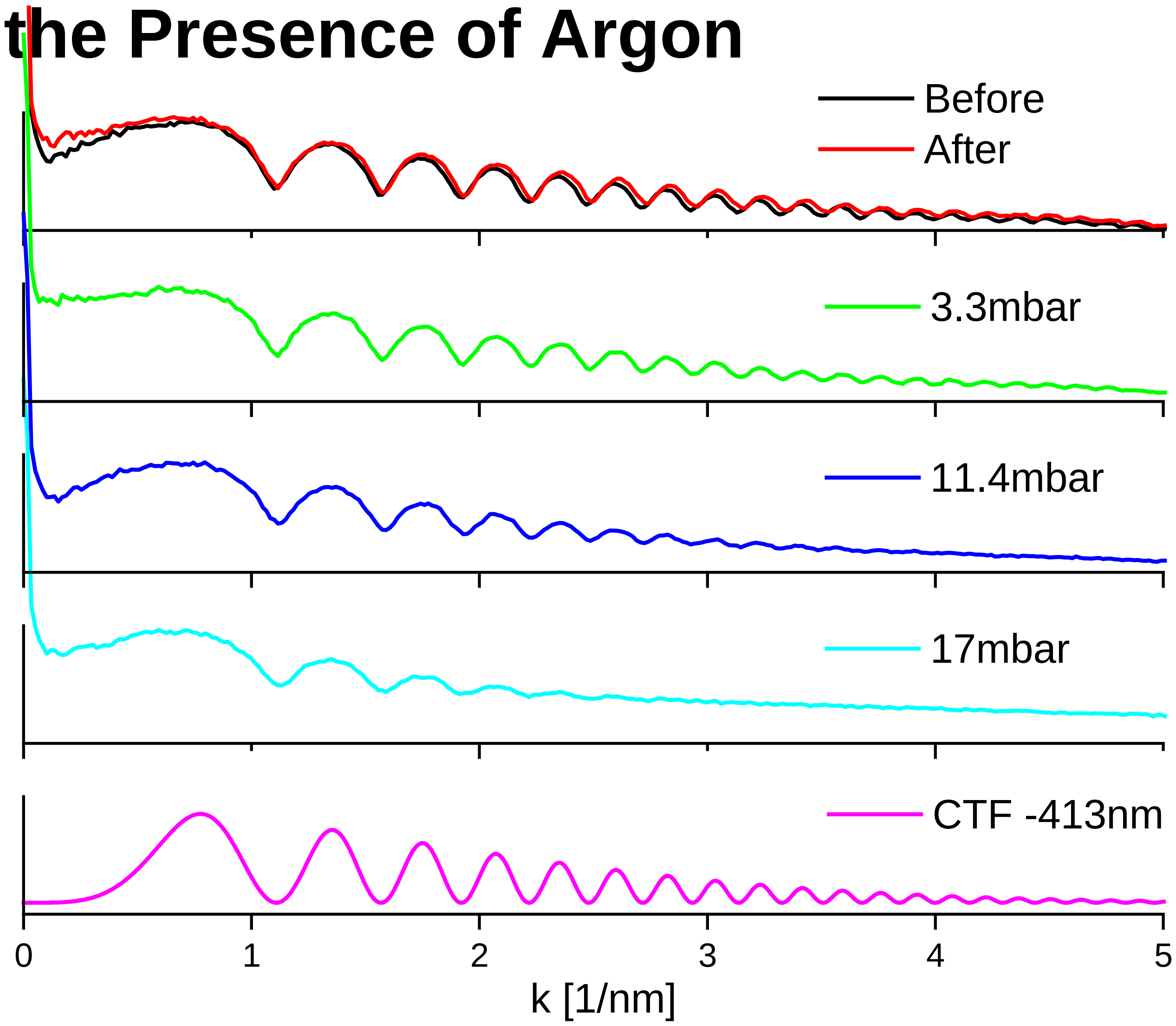




T.W. Hansen and J.B. Wagner, *Microsc. Microanal.* 18, 684 (2012)

Power Spectrum in the Presence of Argon

- Effects of imaging in gas observed from the power spectrum of an amorphous carbon film
- Low pressure: no observable effect (green)
- Damping of the power function increases with pressure (blue, cyan)
- Effects are significantly lower with lighter gas molecules (e.g. H_2, not shown)
- Amorphous carbon film was not significantly damaged (red, after series)



T.W. Hansen and J.B. Wagner, *Microsc. Microanal.* 18, 684 (2012)

Conclusions and Wishes

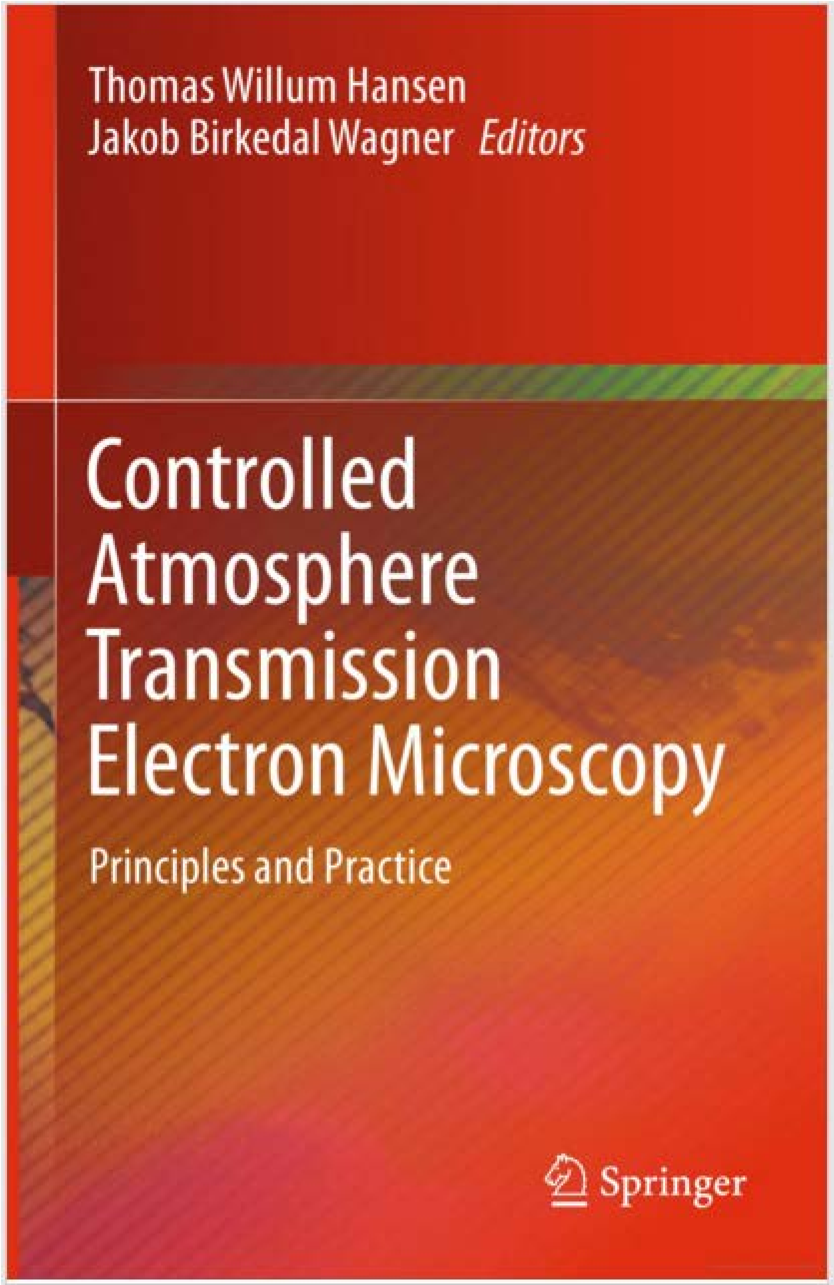
- Improved base pressure
  - Contamination
  - Less oxidizers

- Easier assembly (partly accomplished by new design)
  - Chips still break occasionally

- Sample deposition system
  - Sample should only be on an area where the temperature is uniform (otherwise conversion measurements do not really make sense)

- “Cleaner” MEMS devices
  - MEMS devices often contaminate at room temperature
  - Better reproducibility

- Confine gas to low ΔT region



Thank you for your attention

twh@cen.dtu.dk